DEVELOPMENT OF AN IMPEDANCE-BASED SENSOR
FOR THE DETECTION OF CATALYST COKING IN
FUEL-REFORMING SYSTEMS

by
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ABSTRACT

A novel sensor for detecting the early stages of catalyst coking in fuel reforming systems has been developed. The sensor was manufactured by inkjet printing a colloidal suspension of ceramic powders to create thin (20 µm) catalytic and conductive elements of the sensor. The catalytic elements are composed of a Ni-YSZ cermet. The Ni-YSZ cermet was prepared with a concentration below the percolation limit (20 vol%) of nickel, ensuring a low electrical conductivity. As coke forms on the catalyst material, the nickel nodules in the Ni-YSZ are connected by electrically conductive carbon and the conductivity of the catalyst material increases, indicating coke formation.

Sensors were tested in a 1% ethylene environment to induce coking. The sensor showed a strong response to coking by producing a signal on the order of hundreds of millivolts. The mass of the coke load was determined to be below the detection limit of available thermogravimetric analyzers (TGA) (<10 µg). The coke load was further examined with a field effect scanning electron microscope (FESEM) and was found to be primarily carbon nanofibers. Carbon nanofibers 10-50 nm in diameter connected nickel nodules in the sensors catalyst material resulting in the observed change in resistance.

Sensors were also tested in a dry reforming environment (methane-carbon dioxide). A custom signal amplification circuit was constructed to connect the sensor to an Arduino UNO microcontroller. By interfacing the sensor to the microcontroller, the sensor was able to automatically shut down a carbon dioxide-methane reforming fuel stream when coking conditions were present.
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Catalyst are used in a wide variety of industrial applications. In applications such as fuel reforming or the operation of solid oxide fuel cells (SOFCs), the loss of catalytic activity due to coking is a major concern. As coke forms on the catalyst surface, the active catalyst metal can become occluded by layers of carbon. Extensive coking can cause mechanical failure of the catalyst support, leading to downtime and expensive repairs. A method of detecting coking before significant catalyst damage occurs is therefore desirable. This thesis and accompanying journal article will describe the development of a novel sensor for the early detection of catalyst coking [1].

1.1 The Problem of Catalyst Coking

Fouling by coke formation is a major source of catalyst deactivation in hydrocarbon reforming systems such as solid oxide fuel cells and steam methane reforming applications [2, 3]. Minor coking leads to a loss of catalyst surface area and decreases the efficiency of the reforming process. Severe coking can lead to the mechanical failure of catalyst pellets as coke forms in the crevices of the catalyst material and lifts the catalyst metal from the pellet surface [4, 5, 6].

The damage from coking can force the replacement of the catalyst from a hydrocarbon reforming system. These repairs require replacing expensive catalyst material and the shutdown of the reforming system for maintenance at significant expense. Currently, fuel reforming systems operate with an excess of steam to prevent coke formation, which lowers the efficiency of the system [7]. A sensor which can detect coking in its early stages would allow for tighter control of stoichiometry in the fuel-reforming system. It is therefore desirable to have a sensor to monitor the catalyst for coking in real time. A sensor which could detect coke formation would allow the computer controlling the fuel stream to adjust the
fuel mixture to prevent further coking before the catalyst is catastrophically damaged. This thesis will describe the development of an electrical-impedance-based sensor for the early detection of catalyst coking.

1.2 Prior Work

Previous work on the development of a sensor for the detection of coke formation has taken different forms. Millichamp et. al. [8] used a crystal micro balance with an attached catalyst surface to measure the mass change due to carbon formation on the catalyst surface. Millichamp’s device used a thin disk of a high temperature piezoelectric crystal with an attached catalytic surface to form a crystal micro balance that could be placed in a hot fuel stream. The crystal micro balance measures a change in mass by monitoring the resonant frequency of the thin piezoelectric crystal. Any mass placed on the crystal micro balance will cause a change in the resonant frequency of the crystal. As coke formed on the catalytic surface of the Millichamp’s device, the resonant frequency of the crystal changed due to the added mass on the micro balance. By introducing the micro balance to a fuel stream, Millichamp was able to measure the amount of coke forming on the surface of the sensor.

Müller et. al. [9, 10] used electronic impedance spectroscopy (EIS) to measure the changes in electrical impedance of a catalyst pellet as coke deposited on the surface of the pellet. EIS characterizes materials by sending electrical signals of various frequencies into the sample and analyzing the signal that passes through the sample. By determining the material’s impedance to various frequencies, it is possible to characterize the material’s electrical properties. Muller found that pellets first showed an increase in electrical capacitance at the onset of coking. As coke continued to deposit on the pellet, the capacitative effect dissipated and the electrical resistance of the pellet’s surface decreased. Müller then used thermogravimetric analysis to determine the amount of coke present on the catalyst pellet. By correlating the changing electrical properties of the pellet with the amount of coke present on the pellet, Müller was able to measure the amount of coke present on a pellet’s surface using the pellet’s electrical properties.
Hagen et. al. showed a resistance-based approach was a feasible method to detect soot in the exhaust of a diesel engine due to failures in the engine’s particulate filter [11]. Hagen screen printed gold conductive tracks on a ceramic substrate and measured the electrical resistance between tracks. When no soot was present on the sensor, the resistance was high between the conductive tracks. As soot deposited on the sensor, the conductive carbon in the soot provided electrical connections between conductive tracks and a change in resistance was detected.

Monitoring of the catalyst material has also been shown to be a viable method of assessing catalyst health in a variety of applications [12]. Solid-state ceramic sensors have also been used to measure NO$_x$ concentrations in engine exhaust [13, 14]. The sensor described in this thesis utilizes solid-state ceramic components to detect coke formation.

The sensor described in this thesis is better suited to detecting the onset of coking than previous sensors. While the above sensors can measure milligram amounts of coke, the sensor described in this thesis has a detection limit lower than 10 $\mu$g. The sensor described in this thesis would therefore be better suited for an application where any amount of coking cannot be tolerated, such as a SOFC. The sensor described in this thesis is also simple. The sensor output is a voltage, which can be measured and interpreted easily by a microcontroller with inexpensive electronics. The sensor can also be manufactured easily at a low cost. The sensor can also be added to a fuel reforming system easily because of its small size and the fact that it does not need to be placed inside of a catalyst bed.
CHAPTER 2
SENSOR DESIGN

The physical phenomenon used by the sensor to detect the presence of coke is the electrical conductivity of carbon. The sensor utilizes a non-percolating Ni-YSZ catalyst surface. This surface is similar to the catalysts found in fuel-reforming systems except that it contains a lower concentration of nickel. In a typical supported catalyst, the metal catalyst particles contact each other and form an electrical conduction path through the catalyst material. In the non-percolating Ni-YSZ layer the concentration of nickel is below 20% by volume. This low concentration of nickel prevents the particles of nickel in the catalyst layer from connecting and forming a conduction path, resulting in very high electrical resistance [15]. Sanyal et. al. [15] performed simulations of SOFC electrodes which were used to estimate the percolation limit. Sanyal found that cermets with 20% nickel by volume were at the verge of forming conduction pathways. From Sanyal’s simulation, a 20% by volume cermet has a 0% probability of forming conduction pathways. However, a 30% nickel cermet has a 40% probability of forming conduction pathways. By selecting a concentration of nickel below the percolation limit a cermet with low electrical conductivity is created. As coke forms on the sensor, the nickel nodules are connected by carbon and electrical conduction through the layer increases. As a result of coke formation, the electrical resistance of the layer drops. By monitoring the resistance of the Ni-YSZ layer, it is possible to detect coking in its early stages.

Figure 2.1 shows a schematic of the non-percolating cermet. Nickel nodules are dispersed throughout the YSZ grain structure and do not form electrical conduction paths through the layer. Pores are also present in the layer which allow gas to enter the pore structure and coke to form below the surface of the material. Since the nickel nodules do not form an electrically conductive path across the layer, the electrical resistance of the material is high,
Figure 2.1: Schematic of a non-percolating nickel catalyst (a) Without coking, no conduction paths are present in the Ni-YSZ. The material has high electrical resistance. (b) As filamentous carbon forms conduction paths in the Ni-YSZ, the electrical resistance decreases.

as shown in Figure 2.1a. As coke forms in the catalyst layer, carbon nanofibers grow from the nickel nodules and form electrical connections between nickel nodules. As connections form between nickel nodules, the electrical resistance of the material decreases (Figure 2.1b).

While carbon nanofiber growth has been observed in nickel catalysts, [3, 16, 17, 18] it was not expected to be the dominate mechanism in lowering the resistance of the Ni-YSZ. In the course of evaluating the sensor design, the carbon filaments were found to be more prevalent than expected through electron microscopy, which will be discussed in a later section.

2.1 Sensor Architecture

Inkjet printing has been used successfully to produce ceramics parts including solid oxide fuel cells [19, 20, 21]. To allow the rapid, well-controlled production of samples, the sensor was manufactured using a Fujifilm Dimatix DMP-2800 materials printer. The inkjet printer is capable of printing a variety of different materials including ceramic powders in liquid
suspension. The printer was used to apply lanthanum-doped strontium titanate (SLT) and non-percolating NiO-YSZ to a green partially stabilized zirconia (PSZ) disk. SLT was selected for its electrical conductivity [22, 23, 24, 25]. A green PSZ (Tosoh 3-YB-E) substrate was used to match the rate of contraction of the printed pattern during sintering to prevent sensor warping or cracking. SLT is electrically conductive and was used to provide electrical contacts for the resistance measurements needed. SLT and NiO-YSZ were printed in a pattern to form the desired sensing electrical circuit (Figure 2.2). The disk was then sintered in air according to the manufacturer’s directions. The sensors were first heated at 60°C/hr to 300°C. The sensors were then held at 300°C for 3 hours to burn out the binders in the PSZ used to hold the green disk together during printing. After the burn-out period, the sensors were heated at 270°C/hr to 1450°C and held for 1 hour to allow the sensors to sinter. The furnace was then allowed to cool to room temperature at a rate no faster than 270°C/hr. After sintering, the sensors were placed in a furnace and heated to 600°C at 4 °C/min in a 3% hydrogen atmosphere balanced with nitrogen. The sensors were held at 600°C for 24 hours to reduce the NiO to Ni.

2.2 Architectures Investigated

Three different sensing architectures were tested. The first and simplest design consisted of a single line of Ni-YSZ line connected to four SLT pads. By providing four electrical connections it is possible to utilize the four-point resistance measurement method (Figure 2.3). The four-point resistance measurement allows for accurate measurements of resistance by minimizing the voltage drops due to the resistance of the test leads connecting instruments to the sample. Figure 2.3 shows the circuit used to make four-point resistance measurements. By connecting the voltmeter directly to the test load, the resistance between the current source and the test load is eliminated. Also, since the voltmeter has a high input impedance, the current flowing through the test leads of the voltmeter is small and the voltage drop from the connection to the test load to the voltmeter is small.
Figure 2.2: The different sensor architectures tested (Substrate diameter: 21 mm). Left: A single line of Ni-YSZ connected to four SLT pads to allow for four-point resistance measurements of the Ni-YSZ line. Middle: A quarter-bridge Wheatstone bridge configuration. Right: A half-bridge Wheatstone bridge circuit, which was used for the subsequent tests described in this thesis.

Figure 2.3: The four-point resistance measurement. This method allows for the accurate measurement of resistance in loads with very high resistance. The load to be tested is attached to a constant current source. The voltage drop is then measured across the test load. Since the current through and the voltage drop across the test load are both known, Ohm’s law may be used to determine the resistance. The four-point method allows for accurate measurements of resistance by eliminating the internal resistance of instruments and wire resistance from the measurement.

The four-point resistance measurement method allows for accurate determination of resistances by eliminating the resistance of the wiring and instruments from the measurement. In the four-point method, a known current is put through the test load and the voltage drop across the test load is measured with a volt meter. Since the volt meter has a very high
internal resistance, all of the current except for a negligible amount runs through the test load. Therefore, the voltage drop across the test load measured by the voltmeter can be used in conjunction with Ohm’s law to provide a measurement of the test load’s resistance.

Line type sensors displayed some response to coking conditions in preliminary tests not shown in this document. An architecture that was more sensitive to coke formation was needed. Since the sensor operates by detecting a small change in voltage, the Wheatstone bridge circuit was used as the basis for a new sensor architecture. The Wheatstone bridge circuit converts a small change in resistance into a voltage measurement which can be read easily with a voltmeter [26]. Figure 2.4 illustrates the Wheatstone bridge circuit and its incorporation into the sensor design.

\[
V_{\text{out}} = \frac{R_1 R_3 - R_2 R_4}{(R_1 + R_2)(R_3 + R_4)} V_{\text{in}}
\]

Figure 2.4: The half-bridge circuit. As carbon forms on the Ni-YSZ pads, the resistance of the pads decreases, and \(V_{\text{out}}\) approaches \(V_{\text{in}}\). Inset: An illustration of the sensor wired for a test. \(R_1\) and \(R_3\) are the variable resistors made from non-percolating Ni-YSZ, while \(R_2\) and \(R_4\) are SLT constant-resistance resistors.

2.3 Ink Formulation

In order to use the Dimatix printer to manufacture the sensors, it is necessary to make a suspension of the SLT and NiO-YSZ powders which can be jetted from the printhead. The suspension was developed following the work of Faino et. al. [19]. Since the final viscosity of
the suspension is critical to successful jetting, \( \alpha \)-terpineol was selected as the solvent fluid. The temperature dependent viscosity of \( \alpha \)-terpineol allows the Dimatix printer cartridge heater to hold the ink at an optimal temperature for jetting. NiO-YSZ powder was obtained from Coorstek. SLT powder was obtained from Fuel Cell Materials (lot no. 279-058). The dispersant Solsperse 13940 was used to stabilize the suspension and prevent the solids in the ink from settling. Esprix MX-150 1.5\( \mu \)m poly(methyl methacrylate) (PMMA) particles were used as pore former in the NiO-YSZ ink. After sintering, these particles left pores in the Ni-YSZ cermet with diameters on the order of 1-2\( \mu \)m (Figure 4.5 and Figure 4.6). When not in use, the NiO-YSZ ink was stored in constant rotation on a roller mill to prevent any settling of the NiO powders in suspension and to ensure a consistent ratio of NiO and YSZ was printed on the sensors. Additional details of the ink formulation can be found in [19] and Table 2.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>NiO-YSZ Ink (wt%)</th>
<th>SLT Ink (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-Terpineol</td>
<td>77.6</td>
<td>72.5</td>
</tr>
<tr>
<td>NiO</td>
<td>3.8</td>
<td>-</td>
</tr>
<tr>
<td>YSZ</td>
<td>11.6</td>
<td>-</td>
</tr>
<tr>
<td>SLT</td>
<td>-</td>
<td>27.0</td>
</tr>
<tr>
<td>Solsperse 13940</td>
<td>5.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Pore former</td>
<td>1.3</td>
<td>-</td>
</tr>
</tbody>
</table>

2.3.1 Ink Preparation

In order for consistent printing with the Dimatix materials printer, the ceramic powders and solvents need to be mixed into a stable colloidal solution. In the case of the SLT ink, the preparation is fairly simple. The ingredients in Table 2.1 are measured into a glass vial in the correct amounts for the desired batch size (usually 10 g). 1/4 inch zirconia milling media is added to the ink and the ink is placed on a roller mill overnight to ensure thorough mixing.
The NiO-YSZ ink requires more steps to produce. First, separate NiO and YSZ inks consisting of 15% solids, 6% dispersant in α-terpineol must be prepared. A suspension of 3 wt% pore former and 11 wt% dispersant in α-terpineol must also be prepared. All the suspensions above should be milled overnight to ensure they are thoroughly mixed. Once the suspensions are mixed, they can be combined to create an ink with the desired final composition. Figure 2.5 shows the effect of different ink compositions on the sensor microstructure.

![Figure 2.5: SEM images of catalyst surfaces for inks with and without pore former. The cross sectional view shows a sensor made using ink that contained pore former.](image)

As the NiO content of the NiO-YSZ layer is relatively low, pore former is added to the formulation to promote porosity and high gas transport. Just as the low nickel concentration in the Ni-YSZ layer leads to low electrical conduction, the porosity created by the reduction of NiO to Ni is non-percolating, resulting in sub-optimal gas transport. In early sensors printed
without pore former, the Ni-YSZ pads were still visibly green after 24 hours of reduction at 600°C, indicating a significant portion of the NiO was not being reduced. Un-reduced NiO does not participate in coke formation and therefore does not contribute to the signal the sensor produces. A pore former was therefore necessary to ensure adequate gas transport in the Ni-YSZ layer. The effect of adding pore former can be seen clearly under scanning electron microscope (SEM) (Figure 2.5).

To print sensors using the ink, it is first necessary to create a pattern to guide the printer. Patterns can be created in any image editing software as a bitmap image. The bitmap image uses black pixels to denote a drop of ink and white pixels to denote blank areas. For the printer software to interpret the bitmap image correctly, the image should be set to 1 bit color depth, ensuring that the image is strictly black and white. The image’s resolution must also be matched to the droplet spacing of the printer. For example, if the droplet spacing of the printer is set to 20 µm, then the image resolution needs to be 1270 dpi. If the resolution and droplet spacing are not matched, the printer software will scale the pattern to match the droplet spacing, resulting in a printed pattern with incorrect dimensions. Once a bitmap image of the pattern has been produced, the image is converted using the Dimatix software’s “Import Bitmap” feature. The Dimatix user’s guide provides step-by-step instructions to using the Dimatix software.

In order to conserve printing supplies, it is desirable to reuse the printer’s cartridges for multiple batches of sensors. The cartridges are designed to be disposable and are marketed as single use devices, but they can be easily refilled many times with proper cleaning and treatment. The cartridge consists of two parts, a clear plastic reservoir and a black printhead. The reservoir has four tabs near the cap. The two tabs closest to the cap are security tabs which prevent the reservoir and printhead from being separated after they are put together. Before filling the reservoir, cut the security tabs off using a pair of wire cutters. The reservoir and printhead can then be separated by using a a flathead screwdriver to unclip the remaining tabs from the printhead after printing. When finished printing, the
printhead must be promptly cleaned by flushing alcohol through the printhead with one of the syringes provided with the cartridge fitted with Tygon tubing. Flowing alcohol over the printhead and applying suction with the syringe is also very effective at cleaning the printhead. Whenever printing with a used printhead, use the “Dropwatcher” feature of the printer to inspect the printhead before printing and ensure that the printhead is releasing droplets of ink. If the printhead is not producing droplets, the cleaning cycle of the printer can be run or the cartridge can be removed and cleaned manually.
In systems where a metal catalyst is in contact with carbon-bearing species at temperature, carbon atoms have been observed to form wire-like structures on the order of 1-500 nm in diameter. These structures, known as filamentous carbon or carbon nanofibers, are the result of interesting interactions between particles of the metal catalyst and carbon. The growth of carbon nanofibers has been extensively studied due to both the importance of minimizing nanofiber growth in fuel reforming applications and the interesting properties of the nanofibers themselves. This chapter will discuss the history and current state of research on carbon filaments, the growth and properties of these nanofibers, and the importance of nanofibers in applications ranging from catalyst protection to advanced materials and electrical devices.

3.1 History

The growth of carbon nanofibers was first observed surprisingly early. In 1889 Theophilus Hughes and Charles Chambers patented a process for the “manufacture of carbon filaments” [27]. The process involved running hot coal gas over an iron crucible to produce carbon filaments which were used as elements in light bulbs.

In the 1950s, carbon nanofibers were examined under an electron microscope for the first time by Soviet scientists [28]. Later, carbon filaments were observed growing from iron spots in firebrick by Davis et. al. [29].

For most of the twentieth century, most research on carbon nanofibers centered around their detrimental effects. [30, 31] Carbon nanofibers were observed deactivating catalysts by physically removing the catalyst metal from its support and causing extensive mechanical damage to the catalyst material [4, 5, 6]. Catalysts in pellet form were completely destroyed
by the formation of carbon filaments, and catalyst-lined tubes were cracked by filament growth [30].

In the 1980s, researchers began to notice interesting properties of carbon nanofibers. The high surface area and conductivity of the filaments made them an attractive material for applications ranging from catalyst supports to electrodes to gas storage [30].

3.2 Leading Researchers

Much of the research into the fundamentals of carbon nanofiber growth was completed in the 1970s and 1980s. The foremost experimental researcher during this time period was R.T.K. Baker, who developed a method of observing the formation of carbon nanofibers in-situ by building a reaction cell that could be used inside of an electron microscope [32]. Through use of this technique, Baker was able to observe and characterize the growth rate and activation energy for filament growth [33]. Baker studied the effect of different catalyst materials on the types of carbon nanofibers formed and the rate at which they grew [33, 34].

Meanwhile, a mechanism to describe the growth of carbon nanofibers was developed by several researchers. In 1984, Tibbetts examined the surface energy of filaments to explain the morphology of the filaments [35]. Audier et. al. examined the catalyst particles responsible for filament growth with x-ray diffraction and found a relationship between the crystal structure of catalyst particles and the carbon filaments [36]. Alstrup devised a chemical mechanism [37] explaining the formation and morphology of nanofibers.

Today, most research on carbon nanofibers centers around understanding their growth and properties in an effort to develop applications for their unique properties, rather than minimizing their growth in catalytic systems. Ozkan et. al. examined the mechanical properties of single filaments by placing the filaments in a micro-electromechanical (MEMS) tensile test to measure the elastic modulus and fracture properties of nanofibers [38]. Endo et. al. has examined the properties of carbon nanofibers with an end goal of improving battery technology [39].
3.3 Nanofiber Growth

Nanofiber growth is the result of interactions between a carbon bearing gas and a metal catalyst. Metal catalysts are known to promote the formation of solid carbon deposits [4]. However, if the only affect of the catalyst metal was to promote coke formation, it would be expected that a layer of coke would envelop the catalyst particle, rather than forming an ordered structure as seen in Figure 3.1. In order for a filamentous structure to form, there must be other factors at work as well.

Figure 3.1: An electron microscope image of a carbon nanofiber. The fiber contains a metal catalyst particle at the tip which facilitates filament growth. Note the hollow structure of the filament as well. Reprinted from [35]

In Baker’s 1973 paper [33], the activation energy of nanofiber growth in the presence of various catalyst metals was measured. Baker found a remarkable correlation between the
activation energy for filament growth and the activation energy for carbon diffusion in the corresponding metal. For each catalyst material, the activation energy of filament growth was nearly identical to the activation energy for carbon diffusion. From this observation, Baker concluded that the rate-limiting step in nanofiber growth is the diffusion of carbon through the catalyst material.

From Baker’s observations, the following model for filament growth was proposed. First, carbon-bearing gases pyrolyze on the catalyst metal surface, leaving behind solid carbon. The pyrolysis of most carbon bearing species which are prone to filament formation (C\(_2\)H\(_2\) and C\(_2\)H\(_4\)) is exothermic. The exothermic reaction on one side of the catalyst particle creates a temperature gradient across the particle which drives carbon diffusion. As the catalyst particle becomes saturated with carbon, carbon atoms precipitate out of the cool side of the catalyst particle to form a filament structure. At the same time, some carbon diffuses along the surface of the catalyst particle and forms a graphitic skin on the outer layer of the filament. Finally, if the rate of carbon loading exceeds the rate of carbon diffusion, the catalyst particle will become encapsulated by carbon. Once the catalytic surface is covered by carbon, the catalyst is deactivated and no further growth of the nanofiber is possible. This growth model is shown in Figure 3.2.

However, the thermal gradient model was unsatisfactory in that it did not explain the observation of nanofiber formation from methane and other alkane hydrocarbons, which have endothermic pyrolysis reactions. The endothermic reaction would not produce the thermal gradient to promote diffusion through the particle. A refined model of nanofiber growth was needed [16].

Alstrup reconsidered the driving force for carbon diffusion in his 1988 paper [37]. A schematic of Alstrup’s mechanism is shown in Figure 3.3. Alstrup proposed that the carbon diffusion was caused by a concentration gradient, not a temperature gradient. Alstrup combined results from previous researchers and found that a planar source of carbon just under the surface of the catalyst particle would provide a concentration gradient that would
explain the diffusion process postulated by previous investigators. The source could be a thin layer of metastable carbide just below the surface of the catalyst particle. This metastable carbide layer was supersaturated with carbon due to very fast diffusion through the rough outer surface, or selvage, of the particle. Alstrup called this layer the surface carbide. The concentration of carbon in the surface carbide layer is fixed by the slower diffusion through the particle bulk, which is the rate limiting factor in the filament growth process.

Alstrup’s mechanism was supported by earlier measurements by Gues et. al. which showed that metastable carbides were present during filament growth and that the heat of reaction ($\Delta h_R$) agreed with Alstrup’s theoretical calculations within experimental uncertainty [17, 40]. Gues et. al. detected the presence of metastable carbides by noting changes in the magnetic properties of the catalyst particles during nanofiber production. The heat of reaction is closely tied to the morphology of the carbon nanofibers and will be discussed in the morphology section of this paper.

3.4 Catalyst-Support Interactions

The relationship between the catalyst metal and its support material also plays an important role in the growth of carbon nanofibers [16]. Most metals interact weakly with their support. Nickel and yittria-stabilized zirconia (YSZ) fall into this category. When the metal and support interact weakly, the metal particle is lifted by the growing nanofiber and remains at the tip of the filament. In materials where the metal strongly interacts with the support material, such as ruthenium with a graphite support, the metal remains bonded to the support material and the nanofiber grows by extrusion from the catalyst particle. Schematics of these growing modes are shown in Figure 3.4.

3.5 Effect of Catalyst Composition

Alstrup’s model adequately describes the formation of straight fibers. However, other types of fibers have been observed (Figure 3.5). All of the examples in Figure 3.5 were obtained by using an alloyed catalyst particle. Clearly there is a relationship between the
Figure 3.2: The stages of growth of a carbon nanofiber. a) The metal catalyst particle (M) sits on its support material. b) Introduction of a carbon bearing species ($C_2H_2$) leads to solid carbon formation. c) Carbon diffuses through the catalyst particle and precipitates on the underside of the catalyst particle forming the filament core. Meanwhile, carbon diffuses along the surface of the catalyst particle and forms a graphitic skin around the core of the nanofiber. d) If the catalyst particle becomes encapsulated with carbon, no further filament growth is possible. Reprinted from [16]

Figure 3.3: A schematic of Alstrup’s surface carbide growth mechanism. An atomically thin layer of catalyst metal becomes supersaturated with carbon due to rapid diffusion through the crystal selvage. The growth of the nanofiber is rate limited by the slower diffusion of carbon through the particle bulk. Reprinted from [41]
Figure 3.4: The two growth modes for straight filaments. In catalyst materials which are weakly interacting with their support materials (e.g. Ni-YSZ), the catalyst particle is lifted from the support and remains at the tip of the filament. This mode is known as the whisker-like mode. In systems where the support and catalyst metal are strongly interacting (e.g. Ru-graphite), the extrusion mode is responsible for filament growth. In this mode, the catalyst remains bonded to the support and the filament grows from the metal root. Reprinted from [16]

Rodriguez [42] suggests viewing the process of nanofiber growth in terms of three regions where the crucial processes governing filament growth occur. These regions are:

1. The metal-gas interface
2. The catalyst particle bulk
3. The metal-solid carbon interface

The metal-gas interface determines how carbon is adsorbed by the metal and plays a large role in determining the catalytic activity of the particle. The chemistry of the catalyst bulk determines the solubility of carbon in the catalyst particle and its rate of diffusion.
Figure 3.5: Transmission electron microscope images of various carbon nanofiber types. a) Bidirectional filaments grow from opposite faces of diamond-shaped particles. b) Twisted fibers and c) helical are a product of catalyst particles that rotate during filament growth. d) Branched nanofibers are the result of catalyst particles that fragment during filament growth. Reprinted from [42]

through the catalyst particle, which has been shown to be the rate limiting step in filament growth [16]. Finally, the crystallographic orientation metal-solid carbon interface where the filament is precipitated determines the final structure of the filament.

3.6 Metal-Gas Interface

In order for the carbon to diffuse through the catalyst particle and form a nanofiber, the carbon-bearing gas must first undergo dissociative adsorption at the metal-gas interface. That is, the gas molecules must be broken down into carbon and their other constituent
elements and the carbon must adsorb to the metal surface.

The crystallographic orientation of a catalyst has been know to have a strong affect on the way that carbon bearing gases bond to the catalyst surface and are broken down by the catalyst [43, 44, 45, 46]. For example, Audier [36] showed that metals with a face centered cubic (fcc) structure, the metal gas interface is always composed of the (111) plane and the filament grows along the [110] axis. Nickel catalysts fall into this category. However, in body-centered cubic (bcc) catalysts such as α-iron the metal-gas interface is the (100) plane and the filament is aligned with the [100] axis. Audier’s work determining the crystal axes involved in the gas-metal interface is shown in Figure 3.6.

3.7 Catalyst Particle Bulk

As was stated earlier, the rate-limiting factor in carbon nanofiber growth is the diffusion of carbon through the bulk of the catalyst particle. The composition of the catalyst particle therefore determines the rate at which carbon filaments grow. Different catalyst metals have been shown to have varying activation energies for filament growth [42].

The exact composition of the catalyst particle during filament growth has been a subject of debate among researchers [31, 42]. Some researchers claimed that a high concentration of carbides were needed in the catalyst particle for filament growth [40]. This hypothesis was based on the fact that carbides had been detected in the catalyst particles and it was thought they might be the real catalyst for nanofiber growth [31]. However, it was shown that while carbides were indeed present in catalyst particles, they were only present when the particle was completely deactivated [47].

Alloying the catalyst particle has been shown to greatly increase the activity of the catalyst. The most effective alloys for producing nanofibers are alloys based on copper-nickel solutions [42]. The composition of the bulk particle also plays a strong role in the characteristics of the metal-solid carbon interface, which determines the final morphology of the carbon nanofiber.
Figure 3.6: The structure of the catalyst particle plays an important role in nanofiber formation. Electron microscope images and diffraction patterns showing the crystallographic orientation of the catalyst particles are shown for a) bcc catalysts and b) fcc catalysts. Reprinted from [36]

3.8 Metal-Solid Carbon Interface

At the interface between the metal catalyst particle and the solid carbon of the filament, carbon is precipitated which builds the nanofiber up layer by layer. Different catalysts have been known to produce different morphologies of fibers with varying ratios of graphitic to amorphous carbon [42, 48]

The tendency of a catalyst to produce amorphous or graphitic filaments is tied closely to the catalyst’s surface properties. Figure 3.7 shows the possible interactions between the catalyst and graphite. Catalysts which have a tendency to interact strongly with or
wet graphite in an atmosphere containing hydrogen are more prone to produce graphitic structures rather than amorphous structures [42]. The structure a catalyst will produce can be predicted by studying the wetting angle of the catalyst on graphite. The wetting angle is given by Young’s equation

\[ \gamma_{GS} = \gamma_{MS} + \gamma_{MG} \cos(\theta) \]  

(3.1)

where \( \gamma_{GS} \) is the surface energy of graphite, \( \gamma_{MS} \) is the surface energy of the metal catalyst,

\( \gamma_{MG} \) is the surface energy of the interface between the metal and graphite, and \( \theta \) is the wetting angle. A schematic of the wetting angle is shown in Figure 3.7. When the interaction between the catalyst and the surface is weak, \( (\gamma_{MG} > \gamma_{GS}) \) the wetting angle \( \theta \) is greater than 90° and the catalyst is non-wetting. This type of surface interaction leads to a nanofiber with a mostly amorphous structure [42]. If the interaction between the catalyst and graphite is stronger so that the wetting angle is less than 90°, the catalyst is said to be wetting. In the case of an extremely strong interaction between the catalyst and graphite \( (\gamma_{MS} > \gamma_{GS} + \gamma_{MG}) \), the metal will spread over the graphite surface. Metals which exhibit this type of surface interaction have been known to produce highly graphitic nanofibers. Cobalt, which has a spreading interaction with graphite at temperatures above 400°C, produces highly graphitic
nanofibers. Iron and nickel, though they belong to the same group as cobalt, have weaker interactions with graphite and produce filaments with a significant fraction of amorphous carbon [42].

The dependence of the nanofiber structure on the surface properties of the catalyst metal opens the possibility of predicting the final structure of a nanofiber by observing the interactions of a catalyst and graphite in a reducing atmosphere. Researchers have exploited this relationship to synthesize highly graphitic filaments [48].

3.9 Morphology

The morphologies of carbon nanofibers grown by catalytic methods fall into three main categories, which are shown in Figure 3.8. Platelet-type fibers are produced by interactions between iron catalysts and CO at temperatures below 600°C [50, 48]. When the filament is produced as concentric rings the tubular-type of nanofiber is produced. The basal plane of graphite has a much lower surface energy than the edge planes, so the inner and outer surfaces are made up of the basal plane. The more complicated structure in part c of Figure 3.8 is known as the fishbone structure. The ideal fishbone structure is made up of stacked cups of graphene which expose some fraction of the edge plane to the outer surface of the filament. Most catalytically grown filaments have a structure closer to that of the ideal fishbone. However, both these structures are simplified, ideal models. In reality, carbon nanofibers are not fully graphitic and contain a significant fraction of amorphous carbon [39]. Also, carbon nanofibers do not contain completely perfect graphite crystals. Dislocations and other crystal defects cause irregularities in the filament structure which lead to deviations between models and real nanofibers.

Given the complex nature of the nanofiber morphology, an active area of nanofiber research is centered around developing codes which can more accurately model the growth of carbon nanofibers. Generally, the strategy behind modeling fibers is to break the fiber down into simpler basic structures which can be combined to build up a model fiber. Different researchers use varying schemes for basic building blocks. One method is to treat the fiber as
Figure 3.8: Different types of catalytically grown carbon nanofibers. a) Platelet-type nanofibers are stacks of graphite with the edge planes of the graphitic structure forming the outer edge of filament. b) Tubular-type nanofibers are sheets of graphene rolled concentrically into a fiber. c) Fishbone-type nanofibers consist of sheets of graphene ordered in parallel cones. Reprinted from [49]

3.10 Tibbetts’ Energy Model

The simplified model takes into account the effect of the morphology of the fiber on the heat of reaction ($\Delta h_R$) of the nanofiber growth process. Tibbetts explained why nanofibers are generally hollow tubes by examining the Gibbs free energy of the tubular morphology [35]. By understanding the energy required to form a nanofiber, it is possible to predict the $\Delta h_R$ of filament growth and compare the predictions to observations.

Since the formation takes place under constant pressure and the volume created by filament growth is small, $\Delta h_R$ is taken to be only the energy required to precipitate carbon
from the catalyst particle in the form of a tubular filament. That is

\[ \Delta h_R = U_{surf} + U_{elastic} - U_{chem} \] (3.2)

where \( U_{surf} \) is the surface energy contribution, \( U_{elastic} \) is the elastic strain energy required to bend the carbon atoms into concentric sheets, and \( U_{chem} \) is the energy from the precipitation of carbon out of the catalyst particle.

The first contribution to the free energy of the filament is the surface energy associated with the inner and outer surfaces of the nanofiber. These surfaces are assumed to be the basal plane of graphite. Graphite’s basal plane has a dramatically lower than that of the edge plane. Therefore, the free energy of the filament will be at a minimum and fiber most stable when the exposed inner and outer surfaces of the nanofiber are composed of the basal plane. The surface energy contribution is given by

\[ U_{surf} = \gamma \pi (D_o + D_i) L \] (3.3)

where \( \gamma \) is the surface energy for the graphite basal plane (estimated to be 5.5 J/m² [52]), and \( D_o \) and \( D_i \) are the outer diameter and inner diameters of the fiber respectively. \( L \) is the length of one mole of fiber and is given by

\[ L = \frac{4V_m}{\pi(D_o^2 - D_i^2)} \] (3.4)

where \( V_m \) is molecular volume and is obtained by assuming a density of 2 g/cm².

Next, the elastic energy required to bend the graphene sheets into concentric tubes must be accounted for. Tibbetts derived the following expression for the elastic energy stored in a series of concentric cylinders

\[ U_{elastic} = \frac{1}{12} \pi LE \alpha^2 \ln \left( \frac{D_o}{D_i} \right) \] (3.5)

where \( E \) is the elastic modulus of single crystal graphite (1000 GPa [37]), and \( \alpha \) is the interplanar spacing of graphite.

Finally, the energy from the change in chemical potential due to the diffusion of carbon out of the catalyst particle must be accounted for. The following expression was derived by
Tibbetts by examining the change in volume of the fiber as atoms are added.

\[
U_{\text{chem}} = \frac{\Delta \mu_0 \pi (D_o^2 - D_i^2)}{4\Omega} \tag{3.6}
\]

where \(\Delta \mu_0\) is the change in chemical potential from the diffusion of one carbon atom and \(\Omega\) is the atomic volume of carbon in graphite.

Tibbetts used his model to predict the inner diameter of tubular carbon nanofibers and found good agreement with experimental data for fibers less than 20 nm in diameter [35]. Alstrup later used Tibbetts’ model to predict \(\Delta h_R\) for carbon nanofiber production and also found agreement with experimental data [37].

### 3.11 Significance of Nanofiber Growth

The growth of carbon nanofibers enables the high sensitivity to coke formation displayed by the sensor. A small (<10 \(\mu\)g) mass of carbon will be detected by the sensor because the nanofibers grow rapidly and connect the nickel nodules with a minimal amount of coke. Without the growth of nanofibers, the sensor would need to be coated with a layer of carbon in order for the resistance of the non-percolating Ni-YSZ layer to decrease. Figure 3.9 shows what would occur on the sensor surface if nanofiber growth was not present on the sensor. The sensor would require a larger amount of coke to deposit on the Ni-YSZ before detecting coking, potentially leading to catalyst damage.
Figure 3.9: Without nanofiber growth, carbon would need to form a layer of the surface of the sensor to provide an electrical pathway across the Ni-YSZ pad. A layer of carbon requires more carbon atoms and more time to form than the thin, quickly growing nanofibers. Without nanofiber growth the sensor would take longer to respond to coke formation.
CHAPTER 4

EXPERIMENTAL PROCEDURES AND RESULTS

The test stand used to evaluate the sensors consisted of a sensor holder, electrical test equipment, and a gas delivery system. The sensor holder consisted of a 1 inch Swagelok nut which screwed onto a series of Swagelok adapters. The whole assembly was attached to the end of a 3/16 inch stainless steel tube. The entire assembly was sealed inside a quartz tube for each test. The entire system was heated to ensure the sensor was operating at an elevated temperature. The SLT used to make connections in the Wheatstone bridge circuit loses its conductivity at lower temperatures [25]. Therefore, the sensor must be heated to about 400°C before coke detection is possible. The gas delivery system used three mass flow controllers to control the mixture of forming gas (3.5% hydrogen 96.5% nitrogen) and ethylene to control coking conditions. At the flow rates used in the experiment (0.2 SLPM) the residence time of the gas in the sensor holder was \( \sim 6 \) s. The gas was delivered to the sensor through an alumina tube which ran coaxially inside the 3/16 inch stainless steel tube of the sample holder. The stainless steel tube functioned as the exhaust of the test stand. Gas was also flowed around the outside of the sample holder in the quartz tube to purge any oxygen from the sensor holder. An illustration of the test stand set up is shown in Figure 4.1.

The sensors were powered by a 5 V DC excitation voltage at the electrical contacts shown in Figure 2.4. A 5 V excitation voltage was used because the ultimately the sensor should be interfaced with a microcontroller. Most microcontrollers utilize 0-5 V analog to digital converters, so a 5 V excitation voltage will allow the Wheatstone bridge to output a signal within the range of the analog to digital converter. The 5 V DC excitation voltage was provided by a Fluke PM 2812 DC power supply. Voltage measurements were made by a Keithly 2420 sourcemeter programed to operate as a voltmeter. Output voltage, temperature, and gas-flow data were continuously measured and recorded using National Instruments data
acquisition hardware and LabView software.

Figure 4.1: Illustration of sample holder and furnace setup used to test sensors. The test gases are delivered to the sensor through a non-reactive alumina tube. Gas is also flowed into a quartz cell around the sensor to purge any air from around sensor.

Electrical connections were made by wrapping 24 gage platinum wire over the edge of the sensor and using silver paste to connect the platinum to the SLT of the sensor. The wires were electrically insulated from the stainless steel sample holder by mica washers placed on the front and back of the sensors. The platinum wires were then connected with silver paste to 12 gage silver wires which ran through an alumina tube out of the test cell.

Electrical connections can be difficult to make consistently with silver paste. The platinum wires should be bent to fit the sensor and then held in place by applying silver paste to the SLT and platinum wire. To fully secure the connections, the sensor should be immediately placed into the sample holder. Even when the sensors are carefully connected, there will be some variation in the connections from sensor to sensor. Figure 4.3 shows sensor responses to ethylene exposure and demonstrates that the magnitude and slope of the signal can vary from sensor to sensor.
The sensors were tested by heating the sample to 640°C at 4°C/min under a 0.2 SLPM flow of forming gas. The sensors were left at temperature overnight before testing to ensure the sensors had established a stable baseline voltage output. To produce coking conditions, 0.05 SLPM of 5% ethylene in argon was added to the flow of forming gas to yield a gas flow with an overall gas composition of 1% ethylene, 19% argon, 78% nitrogen, and 2% hydrogen gas. The ethylene flow continued for between 200 to 2000 seconds while the voltage output of the sensor was monitored. Ethylene was selected as a coke precursor because it has been shown to be a significant source of coke formation [53, 54].

4.1 Coking Response

The sensors tested showed a strong response to coking (Figure 4.2, Figure 4.3). The sensor response is generally linear with a total voltage change of between 5 mV and 1400 mV. The slope of the traces produced varied from 0.05 mV/s to 5 mV/s. The difference in the total voltage change and rate of voltage change is due to fabrication inconsistencies from sensor to sensor. While the Dimatix printer produces a consistent layer thickness and placement, the sensors must still be wired into the test stand by hand using silver paste, which introduces inconsistencies in the electrical connections from sensor to sensor. Also, certain batches of sensors had minor contamination issues during sintering. The contamination was a glassy substance which made small (∼0.1 mm maximum) droplets on the face of the sensor that introduced irregularities in the printed pattern of the sensor. Such irregularities would be expected to lower the signal-to-noise ratio of the sensor by adding resistance to the SLT connections on the sensor. Undershoot was observed in some tests (Figure 4.8). The cause of the undershoot shortly after the introduction of ethylene is possibly a gas-phase sensitivity. However, more research is needed to confirm the causes.

Sensor 5’s response was an order of magnitude greater than the other sensors in Figure 4.3. This result is unexpected because all 5 sensors were printed in the same batch simultaneously. Under FESEM, no differences were noticeable between sensor 5 and the other sensors. Additional tests could reveal why sensor 5’s response was so much larger.
A hydrogen chemisorbtion experiment could be used to measure the active catalyst surface area in sensor 5 and the other sensors [55]. Sensor 5 may have a different concentration of nickel in the Ni-YSZ cermet which makes sensor 5 more responsive to coking.

Figure 4.2: Unfiltered coking response voltage traces for several sensors. At time 0, ethylene is introduced to the fuel stream. Additional filtering is useful to help resolve the coking response (See Figure 4.3).

All sensors tested showed an increase in voltage which flattened out after 200-2000 s. The voltage trace closely matches the growth behavior of carbon nanofibers observed by Baker et. al. [33]. As determined previously, the carbon nanofibers grow from a seed particle of the catalyst metal (nickel). Carbon bearing species are pyrolyzed on the particle surface and carbon diffuses into the metal. The carbon atoms diffuse through the metal and form layers of graphitic or amorphous carbon on the opposite side of the particle, resulting
Figure 4.3: Typical coking responses for different sensors. At time 0, ethylene is introduced into the gas stream. The voltage measurements have been smoothed by a 256 point moving average filter ($\Delta t=0.5\,\text{s}$), and shifted to make all traces begin at zero volts. Sensors demonstrated variable responses to ethylene exposure. Variation in the sensor’s response is due to inconsistencies in the manufacturing of the sensors and the electrical connections between the sensor and test equipment. The cause of the non-linearity in sensor 1’s response is unknown. Sensor 5’s response has been reduced by a factor of ten to accommodate the graph axes.

in a carbon filament [16]. Baker observed that a filament grew in length at a linear rate until the catalyst particle at the tip of the filament was completely covered by a layer of carbon. Once the particle was encapsulated in carbon, the catalytic action of the particle was deactivated and the filament ceased to grow. The voltage trace of the sensor’s coking response is consistent with the observed growth behavior of carbon nanofibers by Baker et. al. [33]. While Baker’s experiment and the voltage response of the sensor together is not
sufficient evidence to conclude that nanofiber growth is the cause of the sensor’s response, the fact that a linear increase and similar saturation behavior are observed in both experiments is intriguing. Additional tests are required to examine the relationship between nanofiber growth and the sensor response. Possible experiments are discussed in the future work section of this thesis. Figure 4.4 shows Baker’s observed growth rate for carbon nanofibers. The rate of nanofiber growth and the voltage traces produced by the sensor (Figure 4.3) generally agree with one another. Early sensors not presented in this thesis printed using NiO-YSZ ink where much of the NiO had settled out of the ink before printing displayed no response to ethylene exposure.

![Graph of nanofiber growth rate](image)

Figure 4.4: The growth rate of carbon nanofibers as observed by Baker et. al. in 1973. Baker observed the growth of nanofibers from acetylene on an iron catalyst using in-situ under transmission electron microscopy (TEM). The growth rate of nanofibers observed by Baker is consistent with the voltage response displayed by the sensor (Figure 4.3). Reprinted from [33]

An attempt was made to measure the mass of the coke load on a sensor using a Netzsch STA 409C thermogravimetric analyzer (TGA). The TGA removed the carbon by heating
the sample to 900°C in a hydrogen-steam atmosphere. However, no measurable mass change was observed during the TGA tests. The resolution of the TGA was 10 µg.

4.2 Examination of Catalyst Surfaces

A field-effect scanning electron microscope (FESEM) was used to examine the surface of the coked sensor and obtained the images in Figure 4.6 and Figure 4.7. The images from the FESEM show nickel nodules connected by filamentous carbon on the order of 10-50 nm thick. Filamentous carbon has been observed to form under similar conditions on nickel catalysts [3, 17, 18]. Since the carbon filaments are hundreds of times longer than their diameter, only a small mass of carbon is needed for a measurable decrease in sensor resistance. The result of the wire formation is that the non-percolating nickel surface becomes conductive when a small (<10 µg) mass of coke forms on the surface of the sensor.

Figure 4.5 shows the surface of the non-percolating Ni-YSZ layer of an uncoked sensor. Carbon-free nickel nodules can be seen dispersed throughout the YSZ grain structure. The nickel nodules have an angular appearance. In Figure 4.6 and Figure 4.7 the surface of a coked sensor is shown. Carbon nanofibers can be seen connecting nickel nodules. The fibers on the sensor appear to have a small nickel particle at the tip which catalyzes fiber growth. Similar nanofibers have been observed by other investigators in coked catalysts [3, 16, 17, 18]. Fibers can be seen growing beneath the surface of the sensor through pores (Figure 4.7b), showing that sub-surface connections are occurring. Fibers can also be seen growing towards each other and forming connections (Figure 4.7c) in the space between nickel nodules. The nickel nodules have a smoother appearance in coked samples (Figure 4.6), compared to the more angular shapes observed in uncoked samples, while also having a rougher surface texture due to a layer of carbon on the surface of the nickel nodules in addition to the carbon filaments. This carbon layer was verified using the microscope’s energy-dispersive x-ray spectrometer (EDX).
4.3 Sensor Regeneration

Tests were carried out to determine if the sensor can be regenerated after coking. Coked sensors were exposed to wet forming gas (3.5% hydrogen, 96.5% nitrogen) at 640°C for 24 hours. Water vapor was introduced into the test stand by bubbling the gas through a bubbler at ambient temperature. The sensors were then subjected to a coking test identical to the
original coking test. Sensors showed a similar, but decreased response to coking compared to the original test (Figure 4.8). Upon examining the microstructure of the regenerated sensor under FESEM, nickel nodules were rounder in appearance and farther apart than uncoked samples (Figure 4.9). The change in appearance could be due to either spalling caused by the growth of carbon nanofibers under the nickel nodules as observed in [3], or by smaller particles of nickel sintering together during the regeneration process. After regeneration, the sensor surface showed no connections between nickel nodules and no layer of carbon on the nodules.
Figure 4.7: a) Two nickel nodules connected by a single nanofiber. Multiple shorter fibers can also be seen growing from the nodule on the right. b) Nickel nodules near a pore connected by nanofibers. Nodules inside the pore that have been connected by fibers can also be seen. c) A connection formed by two separate nanofibers meeting between two nickel nodules. The separate nanofibers can be identified by their different diameters. d) Multiple fine connections between three nickel nodules. Using the energy-dispersive x-ray spectrometer (EDX) feature of the microscope, a film of carbon was also detected around the nickel nodules throughout the samples. The carbon film covering the nodules is clear in this picture.
Figure 4.8: Voltage response for a sensor for two coking cycles. The sensor presented in this chart is sensor 4 in Figure 4.2 and Figure 4.3. The sensor was coked with ethylene, regenerated in a wet hydrogen environment at 600°C for 24 hours, and re-coked. The sensor showed similar responses for both cycles. The sensor’s response was slightly smaller during the second cycle. The voltage measurements have been smoothed by a 256 point moving average filter. (\(\Delta t=0.5\,\text{s}\))
Figure 4.9: Left: The surface of a fresh sensor. Right: The surface of a regenerated sensor. More nickel nodules are present on the fresh sensor surface. On the regenerated surface, the nickel nodules are farther apart, and many of the smaller nodules seen in the fresh sensor are missing. Exposing the sensor to multiple coking cycles may degrade the performance of the sensor.
CHAPTER 5  
FEEDBACK CONTROL UTILIZING SENSOR DATA

Although the sensor demonstrated a response to coke formation due to ethylene exposure, a test more representative of a real fuel-reforming system was needed to demonstrate that the sensor enables control of a fuel stream to prevent coking. Two aspects of the tests presented earlier in this thesis are not representative of a real fuel reforming system. First, a mixture of hydrogen, ethylene and inert gases would not be used in fuel-reforming system such as a SOFC due to ethylene’s tendency to form coke [53, 54]. Second, the Keithly sourcemeter used to take voltage measurements is too expensive and complicated to be used for embedded control applications. Therefore, it was necessary to develop a test utilizing a more realistic simulated fuel stream and custom electronics more representative of an embedded control application. Figure 5.1 shows a block diagram of the feedback loop used to represent a more realistic fuel-reforming system in feedback control experiments.

5.1 Control Electronics

In an embedded control, a microcontroller is generally used to read, analyze, and respond to signals provided by sensors [56]. To interface the sensor to the laboratory computer which controls the fuel stream running over the sensor, the Arduino UNO microcontroller was used. The Arduino UNO was selected because it offers a variety open-source programming tools, including National Instruments’ LabView Interface for Arduino (LIFA) toolkit which allows LabView to directly interface with the Arduino UNO. Using LIFA, it was possible to program the Arduino using LabView and process the signal detected by the Arduino with LabView filters and triggering tools. Once a coking signal was detected, LabView could then automatically shut down the fuel stream to stop coking.

In order to use the Arduino, it was necessary to develop a custom circuit to measure the bridge voltage of the sensor and amplify the analog signal to a level suitable for the Arduino’s
Figure 5.1: The system used to perform feedback control experiments with the sensor. When coking is detected, the sensor’s signal is conditioned by an amplifier circuit, converted to a digital signal and processed by the Arduino microcontroller, and responded to by the fuel-mixing computer.

Figure 5.2 shows the circuit which was used to prepare the analog signal for the Arduino. The circuit was designed around the Texas Instruments INA 125 instrumentation amplifier. The INA 125 receives two voltages as inputs, in this case the voltage at each side of the sensor’s Wheatstone bridge, and outputs a voltage with the magnitude of the difference between the two input voltages.

In order to use the INA 125 and Arduino to read and analyze the signal from the sensor, the offset voltage from the sensor must be compensated for. In an ideal bridge circuit, all the resistive elements have matched resistances so the bridge output is 0 V (Figure 2.4). If the resistive elements are not properly matched, the bridge will output a voltage. In the case of the sensor, SLT and the Ni-YSZ cermet have very different electrical resistances. The differences in electrical resistance lead to an imbalanced bridge and an offset voltage. In the
Figure 5.2: The amplifier circuit used to interface the sensor to the Arduino microcontroller. The Texas Instruments INA 125 instrumentation amplifier was used to determine the output voltage of the sensor’s Wheatstone bridge. The Arduino’s pulse width modulation (PWM) feature was used to provide an input bias to correct the bridge offset voltage resulting from the difference in electrical resistance between the SLT and the Ni-YSZ elements of the sensor.

In the case of the sensor, the offset voltage is enough to saturate the INA 125 amplifier. If the offset voltage was not corrected, the INA 125 would not be able to resolve any signal from the sensor.

In order to correct the offset voltage, the input bias nulling method was used. The input bias nulling method utilizes an adjustable voltage source connected to the input of the instrumentation amplifier to cancel whatever offset voltage is produced by the bridge circuit [57]. The voltage source used was the Arduino’s pulse width modulation (PWM) feature. PWM allows the digital Arduino to output a simulated analog voltage by rapidly switching a 5 V source on and off while varying the duty cycle. In order to prevent a ripple voltage from appearing in the sensor’s signal, the PWM voltage was filtered through a low pass filter.
The resulting voltage was connected to the inverting input of the INA 125 (Figure 5.2). Figure 5.3 shows the circuit connected to the Arduino in order to read the sensor output.

Figure 5.3: The circuit used to interface the sensor to the Arduino. The circuit was prototyped on a breadboard Arduino shield obtained from Jameco Electronics. The circuit powers and connects a Texas Instruments INA 125 instrumentation amplifier to the sensor. The Arduino’s PWM output is connected to the inverting input of the INA 125 to cancel the offset voltage due to the sensor’s unbalanced bridge circuit. The output of the INA 125 is then sent to the Arduino’s analog to digital converter.

5.2 Dry Methane Reforming Fuel Stream

Coking is caused by a fuel mixture which contains more carbon than can be oxidized by the oxygen in the fuel [58]. Figure 5.4 shows fuel stream compositions which will form coke at equilibrium.
While the ethylene-hydrogen mixture used in preliminary tests of the sensor was able to generate coke, the mixture was not very representative of a real fuel stream. Ethylene’s tendency to form coke makes it undesirable in fuel-reforming systems [53, 54]. A new testing regime was developed to simulate a dry methane mixture. Methane dry reforming converts methane and CO$_2$ into hydrogen and CO through the following reaction [59]:

$$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$$
Dry reforming leads to coke formation when there is insufficient oxygen in the fuel stream to oxidize the carbon and form CO. Coke formation occurs through four chemical reactions [59]:

\[
\begin{align*}
2 \text{CO} & \rightleftharpoons \text{CO}_2 + \text{C} \\
\text{CH}_4 & \rightleftharpoons 2 \text{H}_2 + \text{C} \\
\text{CO} + \text{H}_2 & \rightleftharpoons \text{H}_2\text{O} + \text{C} \\
\text{CO}_2 + 2 \text{H}_2 & \rightleftharpoons 2 \text{H}_2\text{O} + \text{C}
\end{align*}
\]

In the above reactions, coke formation is a result of the C species being left on the catalyst surface rather than being oxidized to form CO.

A dry reforming fuel stream was selected because of its representative nature and the minimal setup required in the laboratory. A steam-methane reforming experiment could be carried out. However, in a laboratory experiment it is difficult to introduce sufficient steam into a fuel stream because the gas lines must be heated and temperature controlled. Water vapor’s tendency to condense in the gas lines makes accurate control of the steam-methane ratio difficult to maintain. However, methane-CO\(_2\) mixtures have been shown to behave similarly to steam-methane mixtures in SOFCs [60]. Figure 5.5 shows the sensor’s response to excess methane in a methane-CO\(_2\) environment. When the CH\(_4\) and CO\(_2\) are mixed in a safe composition (Figure 5.4 A), no coking is detected. When the mixture is changed to contain excess methane (Figure 5.4 B), the sensor detects the onset of coking.

### 5.3 Feedback Control Results

A test was carried out (Figure 5.6) to determine if the sensor was capable of automatically controlling a fuel stream. The sensor’s signal was read by the Arduino and analyzed by LabView’s moving average and basic trigger tools. A 16 point moving average filter (\(\Delta t=.5\) s) was used to smooth the signal read by the Arduino. The smoothed signal was analyzed by LabView’s basic trigger VI. The basic trigger VI monitors a signal and changes a boolean variable from “False” to “True” when the signal reaches a specified level. In this case, the
amplifier bias nulling voltage was set using the Arduino’s PWM such that the baseline signal when no coke was present was 2.5 V. The basic trigger VI was then programmed to activate when the absolute value of the difference between the signal and the 2.5 V baseline was greater than 1 V.

Figure 5.7 shows the LabView VI used to provide filtering and triggering. Through use of the LIFA LabView plug in, LabView is able to receive a voltage signal from the sensor. The voltage signal is smoothed by a 16-point moving average filter. The smoothed signal can then be analyzed by the basic trigger VI. The basic trigger VI changes its output from
“False” to “True” when the signal reaches a certain level. To make the most use of the available 5 V measurement range, the Arduino’s PWM feature was in conjunction with the amplifier circuit to produce a baseline signal of 2.5 V. By centering the baseline signal in the analog to digital converters range, the signal may increase or decrease without saturating the converter.

The sensor was exposed to the specified safe mixture of CO$_2$ and CH$_4$ at 640°C. The sensor did not produce any coking signal at the safe composition. When excess CH$_4$ was added to the mixture, the sensor detected coking and activated the basic trigger VI. LabView then shut down the gas flow in response. Figure 5.6 shows the result of the closed-loop control test. Before time 0, the sensor is exposed to only CO$_2$. At time zero, the safe composition of
Figure 5.7: The VI used to analyze and respond to the sensor’s signal. The Arduino reads the signal from the sensor. The voltage signal read by the Arduino is smoothed by a 16-point moving average filter. The smoothed signal is then analyzed by the basic trigger VI. If the signal deviates from 2.5 V by more than the specified trigger level (1 V), then a “True” signal is sent to a case structure which controls the operation of the MFCs. When the “True” signal is received, the MFCs turn off.

methane and CO$_2$ is introduced to the sensor (Figure 5.4 point A). At around time 150 s, the coking mixture of methane and carbon dioxide is introduced to the sensor (Figure 5.4 point B). The gas flow is seen to stop immediately when the trigger level is reached. The time elapsed from when the sensor was exposed to coking conditions and when the fuel stream was shut down automatically was 130 s.
CHAPTER 6
CONCLUSIONS

During the course of the research leading to this thesis a new sensor for detecting coking in fuel-reforming systems was developed. The sensor is able to detect minute (<10 µg) amounts of coke by responding to the growth of carbon nanofibers at the onset of coking. FESEM images confirmed that carbon nanofiber growth was the dominant growth mechanism of carbon on the sensor surface. To the best of our knowledge, this is the first sensor to utilize the growth of carbon nanofibers as a sensing mechanism. The sensor was able to be operated with a microcontroller, as it would be in a real world embedded control scenario. When exposed to a coking methane-CO$_2$ environment, the sensor was able to detect coke formation and shut down the fuel stream in 130 s. Such a sensor has applications for protecting fuel-reforming systems such as SOFCs by detecting the onset of coke formation and shutting down the system before extensive coking damage can occur.

6.1 Future Work

While the sensor described in this thesis was shown to be capable of closed-loop control, additional work is needed to refine the sensor to a market-ready device.

A study comparing the growth rate of carbon nanofibers and the sensor response would be valuable in confirming that the sensor’s response is due to carbon nanofiber growth. Baker’s experiments [33] focused on the growth of single nanofibers. The sensor’s response is the result of many nanofibers growing simultaneously. A simulation of nanofiber growth on a non-percolating Ni-YSZ cermet could show how the resistance of the Ni-YSZ changes as nanofibers grow. It is currently unknown how the growth rate of single nanofibers can be correlated to a change in resistance in the Ni-YSZ pad. A simulation investigating the average distance between particles that must be bridged by a nanofiber, how quickly nickel nodules
can be connected by nanofibers, and the effect of nickel concentration on the predicted sensor response could provide valuable insight into how the sensor operates.

In order to improve the sensor’s ability to intelligently control a fuel reforming system, more tests are needed to determine if the flow rate over the sensor has any effect on the sensor signal. Changing the flow rate will in turn change the residence time of the gases in contact with the sensor. The effect of the residence time on the sensor signal is currently unknown. Also, the sensors presented in this thesis exhibited variable lag times between when a coking fuel stream was introduced to the sensor and when a coking signal was detected. Changing the residence time of the gases on the sensor may provide insight into what causes the lag time. If the flow rate is too low over the sensor, the gas composition at the sensor surface may not be the composition expected until sufficient time has passed to allow the gases in the test stand to be exchanged. A faster flow rate would result in a shorter lag time if this scenario were true.

Other improvements to the sensor could be made by changing the materials used to manufacture the sensors. Currently, the sensor must operate at elevated temperatures due to the use of SLT for making the electrical connections in the Wheatstone bridge circuit. SLT’s conductivity decreases at lower temperatures [25], so the sensor is unable to produce a signal for temperatures less than about 400°C. Researchers have previously printed gold and platinum onto ceramic substrates [11]. The use of a metallic conductor would reduce the resistance of the electrical connections in the Wheatstone bridge circuit and eliminate the temperature dependent conductivity of SLT. Eliminating temperature dependent resistances in the sensor is desirable because any change in resistance in any part of the Wheatstone bridge circuit will appear as a drift in the sensor output. Eliminating drift would allow for the coking signal to be resolved more easily. A metallic conductive element on the sensor would also allow the sensor to operate at lower temperatures.

The amount of pore former in the NiO-YSZ ink could also be optimized. When pore former was added to the ink, a large improvement in sensor response was observed. Opti-
mizing the pore former concentration in the NiO-YSZ ink could lead to greatly improved sensor response.

The sensor could also be improved with a more intelligent control scheme. Currently, the sensor uses a simple trigger level to detect when a coking signal is present. The drawback of this method is that a false positive could be detected if the sensor's output drifts due to a change in temperature or other factors. A more sophisticated control program could watch for rapid changes in sensor output rather than any change in output. From the experiments described in this thesis, a coking signal manifests itself as a rapid change in voltage rather than a slow drift. Experiments to characterize the sensor’s response to temperature changes and changes in flow rate would help determine the software design necessary to detect a coking response.

Other characterization experiments could include a study of how the concentration of nickel in the Ni-YSZ affects the sensor sensitivity. By optimizing the concentration of nickel in the Ni-YSZ cermet, greater sensitivity could be achieved by minimizing the distance between nickel nodules in the cermet that must be bridged by nanofibers. The time required to bridge the gaps between nickel nodules could be investigated by exposing sensors to coking conditions for set periods of time. After the time has expired, the test cell would be purged with inert gas to stop nanofiber growth. The different intervals would then be examined under FESEM to see how many connections are formed over time.
REFERENCES CITED


