DEVELOPMENT AND CHARACTERIZATION OF AN IMPEDANCE-BASED CARBON SENSOR FOR THE DETECTION OF CATALYST COKING IN STEAM-METHANE AND DRY-METHANE REFORMING SYSTEMS

by

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ABSTRACT

A carbon sensor designed to detect the early stages of catalyst coking in methane reforming systems has been developed. The sensor is similar to the one developed by Wheeler et al., but it has been redesigned to reduce unwanted gas-phase response and increase coking response in methane reforming environments. The sensor comprises of a Wheatstone bridge with two catalytic, non-percolating cermet resistive elements printed using an inkjet printer. As carbon begins to grow on the catalytic surface, the electrical conductivity of the catalytic material increases, which results in a change in the continuously monitored bridge output voltage. By replacing SLT (strontium-doped lanthanum titanate) as the non-catalytic half of the Wheatstone bridge, gas phase response is reduced. In the existing design, all four of the bridge elements are YSZ (yttria-stabilized zirconia) based and voltage change due to gas-phase composition is reduced by a factor of 10 from a SLT-based sensor.

Steam and dry reforming tests were conducted at 600 °C with low steam-to-carbon and CO₂-to-carbon feed ratios to promote coking. The sensor showed strong response (on the order of several hundred millivolts) to carbon formation on the surface under both of the reforming environments studied. Field-emission scanning electron microscope (FESEM) imaging showed surface catalyst (Ni) particles encapsulated in films of carbon. Sensors were regenerated using steam and then demonstrated similar, but smaller, responses to the same coking conditions. Investigation of regenerated sensor surfaces showed the presence of fewer catalyst sites compared to fresh sensors, indicating that the loss of nickel particles leads to a degradation in the sensor response.
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Catalyst are used all around us. Most of the industrially important chemical processes involve catalysis at some stage of production. Catalysts are especially important in fuel reforming systems, such as steam reforming of methane, where a big concern is the loss of active catalyst surface due to carbon deposits formed as byproducts of the reforming reactions, i.e. catalyst coking [1]. This thesis is aimed at describing a carbon sensor which has been developed to detect the early stages of catalyst coking in steam-methane and dry\(\text{CO}_2\)-methane reforming systems.

1.1 The Problem of Catalyst Coking

Catalyst coking can lead to a myriad of problems. Initially, coking leads to a loss of active catalyst surface area, and it eventually contributes to the complete mechanical failure of the catalyst pellets, which usually consists of a catalyst metal and a support material [2, 3, 4]. Severe damage to the catalyst forces its replacement. This is an expensive and time consuming process. Therefore, a sensor that could detect the presence of conditions conducive to the formation of harmful carbon deposits on the active catalyst surface is highly desirable.

1.1.1 The Significance of Methane Reforming

Steam reforming of methane is a mature industry. It has been around for many decades. Steam-methane reforming continues to be the primary and most economical source of hydrogen and syngas, both needed in a variety of chemical and petrochemical processes [5, 6, 7, 8]. Hydrogen also promises to replace fossil fuels at large in the future, and while several other techniques for hydrogen and/or syngas production (photochemical and photobiological processes, etc.) exist, they are still in the early stages of development and implementation;
therefore steam reforming will continue to be an important industry for quite some time [9]. Nickel is the most commonly used catalyst in methane reforming processes, and catalyst deactivation due to coking is a major concern in methane reforming systems [10, 11, 12]. Coking of the catalyst pellets decreases the active surface area of the catalyst, thereby decreasing the efficiency of the reforming process. While studies have been devoted to developing novel catalysts that are more resistant to coking, their widespread implementation in the industry remains largely absent due to cost, performance, and availability [10, 13, 14, 15, 16]. The dominant industry practice to avoid coking of the nickel catalyst in the steam methane reforming process is to operate under excess steam at the expense of reforming efficiency [10].

Dry or CO\textsubscript{2} reforming of methane, although not a strong industry at this time, promises to be an exciting industry whereby CO\textsubscript{2} and CH\textsubscript{4}, two major greenhouse gases can be converted to hydrogen [17, 18]. Loss of catalyst activity due to coking is also a major concern in the dry-methane reforming process. Therefore, due to the importance of the methane reforming industry, the impedance-based carbon sensor described in this thesis has been designed specifically to detect early stages of coking in steam-methane and dry-methane reforming processes. The sensor signals will allow for better control of the stoichiometry of the reactants used in a reforming process, while avoiding feed mixtures that are prone to coking of the catalyst.

1.2 Previous Work

Wheeler et al. developed an impedance-based sensor that was successfully able to detect trace amounts (<10 $\mu$g) of carbon deposits formed on an active nickel surface exposed to coking conditions in a reducing environment by reacting ethylene and hydrogen [19]. The sensor, manufactured using a variety of ceramic powders, utilized the fact that the formation of carbon deposits, usually in the form of nanowires, significantly changes the electrical conductivity of a non-percolating layer of catalytic nickel [20]. Figure 1.1 illustrates the mechanism. The change in the electrical conductivity was monitored using a Wheatstone
bridge circuit consisting of nickel-YSZ (yttria-stabilized zirconia) and SLT (strontium-doped lanthanum titanate) elements. So it was possible to monitor the early stages of the coking of the catalyst in real time.

Building upon the work of Wheeler et al. a very similar coke sensor that can function optimally under conditions typical in the steam-methane and dry-methane reforming processes has been fabricated and characterized.

Figure 1.1: Schematic of a non-percolating nickel catalyst layer. (a) In the absence of carbon, conduction paths are scarce and the electrical resistance is high. (b) & (c) Conduction paths open up when carbon deposits appear on the surface. Carbon filaments are abundant as in (b) in reducing environments. Films of carbon on the nickel surface are more prevalent as in (c) in oxidizing environments and filamentous carbon is rare.
1.3 Summary of Improvements to Sensor Design and Performance

The sensor’s gas-phase response has been reduced by an order of magnitude by replacing the non-catalytic SLT bridge elements with YSZ. SLT was also used as the interconnecting material for the bridge elements, which been replaced by silver. Gas-phase response was a huge problem because it was often greater than any coking response and several-hundred millivolts in magnitude.

The nickel loading of the sensor’s catalytic bridge elements has been increased to improve the response due to carbon formation in methane reforming environments. Previously, sensors were primarily tested in a reducing ethylene-hydrogen environment. Under these conditions carbon nanowires formed abundantly (Figure 1.1). However, in the absence of ethylene and in the oxidizing environments of steam-methane and dry-methane reforming, carbon nanowires were extremely rare and the bulk of the carbon deposits took the form of films encapsulating the catalyst particles. A reasoning for this observation is provided later. The carbon films do not grow as far away from the nickel particles as the nanowires do. This results in opening up fewer conduction paths between nickel particles as an effect of coking and, consequently, a smaller change in the bridge output voltage. The proximity of the nickel particles was decreased by increasing the nickel loading in the catalytic bridge elements. This resulted in an improvement on the coking response of the sensor.
CHAPTER 2
LITERATURE REVIEW OF METHANE REFORMING AND CATALYST COKING IN REFORMING ENVIRONMENTS

Fossil fuels have come to be extremely popular in the last century. They are, however, non-renewable. In addition, pollutants emitted by fossil fuel based energy systems, such as: CO$_2$, CO, SO$_x$, NO$_x$, etc., are a major concern for the long-term stability of the earth’s environment [21]. Hydrogen is a fuel free of carbon and oxidizes to water after combustion. As energy sector pushes to find renewable alternatives to fossil fuels, hydrogen is expected to play a very important role because of its ability to supplement any energy stream and apply to any load [22].

Steam reforming of methane is the major industrial process for the manufacture of hydrogen (and synthesis gas). Although estimates vary, steam-methane reforming is understood to account for more than 80% of the world’s hydrogen production [23]. A process for the conversion of natural into hydrogen using steam was first described by Tessie du Motay and Marechal in 1868 [5], and the first industrial process for steam reforming of methane was implemented in the 1930s [11]. Since then, several other processes for hydrogen production have also emerged.

The main processes for hydrogen production and their development/implementation status have been summarized in Table 2.1. Some of these processes have reached maturity for commercial exploitation: (a) steam reforming of natural gas; (b) catalytic decomposition of natural gas; (c) partial oxidation of heavy oils; (d) coal gasification; and (e) steam-iron coal gasification. Other processes, such as thermochemical, photochemical, photoelectro-chemical and photobiological processes are being explored at the research and development stage.
Table 2.1: Summary of main hydrogen production processes [24].

<table>
<thead>
<tr>
<th>Production process</th>
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<tr>
<td>Steam reforming of natural gas</td>
<td>Mature</td>
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<tr>
<td>Catalytic decomposition of natural gas</td>
<td>Mature</td>
</tr>
<tr>
<td>Partial oxidation of heavy oil</td>
<td>Mature</td>
</tr>
<tr>
<td>Coal gasification</td>
<td>R and D Mature</td>
</tr>
<tr>
<td>Steam-iron coal gasification</td>
<td>R and D</td>
</tr>
<tr>
<td>Water electrolysis</td>
<td>Mature</td>
</tr>
<tr>
<td>Thermochemical cycles (pure)</td>
<td>R and D</td>
</tr>
<tr>
<td>Thermochemical cycles (hybrid)</td>
<td>R and D</td>
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<tr>
<td>Photochemical processes</td>
<td>Early R and D</td>
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<tr>
<td>Photoelectrochemical processes</td>
<td>Early R and D</td>
</tr>
<tr>
<td>Photobiological processes</td>
<td>Early R and D</td>
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2.1 Fundamentals of Steam-methane Reforming

The steam-methane reforming process for producing hydrogen can be divided into three sections: reforming, water-gas shift, and CO₂ removal. A schematic flowsheet for a conventional steam-methane reforming process is shown in Figure 2.1. A picture of a real plant is also shown in Figure 2.2.

In the reformer, the following global reactions take place:

\[
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \quad (2.1)
\]

\[
\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2 \quad (2.2)
\]

These reactions are endothermic (\(\Delta H^0_{298} = 206\text{kJ/mol}\) and \(\Delta H^0_{298} = 165\text{kJ/mol}\), respectively) and are typically carried out at a temperature of 600–1000 °C and a pressure of 5–15 atm over a nickel-based catalyst [26]. The steam-to-carbon ratio varies from 3:1 to 6:1, depending on the age of the reformer, with newer reformers being able to operate at the
Figure 2.1: Flowsheet for a conventional steam-methane reforming process. Adapted from [11].

Figure 2.2: A steam reforming plant. From [25].
The effluent gas of the reformer typically contains around (mol %): 76% H\textsubscript{2}, 13% CH\textsubscript{4}, 12% CO, and 10% CO\textsubscript{2} on a dry basis [27].

The products of the reformer are then fed to the water-gas shift reactor, where the following reaction occurs:

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\]  \hspace{1cm} (2.3)

Reaction 3.3 is moderately exothermic ($\Delta H_{298}^0 = -41\text{kJ/mol}$) and is typically carried out at temperatures much lower than the reformer.

Finally, pressure swing adsorption technology is used to purify the product to the desired level. Depending on the purity of hydrogen required, the pressure swing adsorption process can dictate the cost requirement of the overall steam-methane reforming process.

### 2.2 Steam-methane Reforming in Solid Oxide Fuel Cells

Fuel cell technology is a rapidly growing industry. Fuel cells have the potential to become one of the most important energy conversion tools because of their ability to directly convert the chemical energy of a fuel to electrical energy, and their benefits concerning fuel efficiency, emissions, maintenance and noise pollution over conventional systems [28]. For stationary applications and combined heat and power generation systems solid oxide fuel cells (SOFCs) are usually preferred to other types of fuel cells [29]. SOFCs typically operate in the temperature range 700–1000 °C and utilize hydrogen containing gas mixtures as the fuel. Oxygen from the air is used as the oxidant. In SOFC applications internal steam-methane reforming can be utilized to make the hydrogen fuel. A typical SOFC anode support contains nickel, which can be used as a catalyst for the steam reforming of methane [30]. The operating temperature range of an SOFC is also suitable for methane reforming [31, 32]. The advantages of internally reforming methane in SOFCs have been summarized by Ahmed et al. [33]. The heat generated from the fuel cell operation can provide the endothermic heat required for the steam reforming reaction and the required heat is about half of that produced in the SOFC stack under typical operating conditions. Less steam is
required overall because part of the steam required for the methane reforming process can be obtained directly from the steam generated by the fuel cell. The reforming reaction can proceed beyond the thermodynamic equilibrium by Le Châtelier’s principle because of the continuous consumption of hydrogen by the fuel cell. The cooling requirement of the SOFC, which is usually achieved by flowing excess air through the cathode, can be reduced by 40-50% by when internal steam-methane reforming is utilized. Also, a more evenly distributed supply of hydrogen can be achieved, which can potentially lead to a more even temperature distribution in the SOFC stack. With no separate external reformer, significant reduction in capital investment and operating costs can be achieved. Finally, SOFCs equipped with internal reformers will have the potential to offer faster response to load variations.

2.3 Overview of Dry-methane Reforming

Catalytic reforming of methane with carbon dioxide (dry-methane reforming) to produce synthesis gas has been proposed as a promising technology for utilizing two greenhouse gases: carbon dioxide, and methane [18]. The synthesis gas that is produced as a result of dry-methane reforming has a relatively high carbon monoxide content, which is desirable in the synthesis of valuable oxygenated chemicals [34, 35]. Unfortunately, carbon dioxide reforming of methane, unlike steam reforming of methane, is not an established industry at this time. Fischer and Tropsch suggested dry-methane reforming as an alternative to steam-methane reforming in 1928 [18].

The global reaction for CO\(_2\) reforming of methane is:

\[
\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2\text{CO} + 2\text{H}_2 \tag{2.4}
\]

The reforming reaction is highly endothermic (\(\Delta H_{298}^0 = 247\text{kJ/mol}\)) and is favored at low pressures and high temperatures. Note that the H\(_2\) to CO ratio is 1:1, whereas a 3:1 ratio is obtained by steam reforming of methane (reaction 2.1). So the combination of the two reforming processes can greatly widen the utility of syngas in methanol or Fischer-Tropsch synthesis where a H\(_2\) to CO ratio of 2:1 is required [36]. During dry-methane reforming, a
reverse water-gas shift reactions also occurs simultaneously.

2.4 The Steam-methane Reforming Catalysts

Sehested summarized four challenges of nickel catalyst in steam-methane reforming applications [25]. These are: the activity of the catalyst, sulphur poisoning of the catalyst, carbon formation on the catalyst, and sintering of the catalyst. The catalyst activity is important because the reforming catalyst must have sufficient activity to equilibrate the reaction mixture in the design catalyst volume. Sulfur is a strong poison for nickel catalysts and blocks the active nickel sites. The feedstock in methane reformers typically contains some sulfur. Although the feedstock is usually desulfurized, some sulfur may reach the surface of the nickel catalyst. Therefore, the sulfur adsorption capacity of steam-reforming catalysts is an important parameter. Carbon formation on the catalyst surface during reforming may block the active nickel surface, increase the pressure drop in the catalyst pellet, crush the pellets, and even form at the inner perimeter of the reforming tubes resulting in a lower heat transfer and overheating. Therefore it is important to understand the conditions which can reduce the rate of carbon formation during reforming. Nickel particles in the catalyst may grow while being exposed to the high temperatures of the reforming process. This process is called sintering. Sintering will results in the loss of active catalyst surface area. Loss of catalyst support area by support collapse due to thermal cycling can also lead to sintering [37]. Operating at high temperatures and using excess steam can dramatically increase the sintering rate [38].

2.5 Coke Formation During the Steam-methane Reforming Process

The high operating temperature requirements of the reforming processes illustrated in the previous sections introduce an array of problems. The thermal stability of the catalyst is one of them. At high temperatures, steam has a propensity for sintering of the catalyst and support materials [39, 40]. However, the largest problem is the formation of coke on the catalyst surface.
Steam and CO\textsubscript{2} reforming of methane results in carbon formation by the Boudouard reaction [41, 3].

\[
\text{2 CO} \leftrightarrow \text{CO}_2 + \text{C(s)} \tag{2.5}
\]

Methane cracking can also lead to carbon formation.

\[
\text{CH}_4 \leftrightarrow \text{C(s)} + 2 \text{H}_2 \tag{2.6}
\]

Carbon monoxide can also react with hydrogen to form carbon deposits.

\[
\text{CO} + \text{H}_2 \leftrightarrow \text{C(s)} + \text{H}_2\text{O} \tag{2.7}
\]

In the temperature range of 550–700 °C carbon will be formed by a combination of the three reactions described above [18]. Formation of coke by the Boudouard reaction becomes less favored with increasing temperature, but coke formation by methane cracking becomes increasingly important at higher temperatures and contribute to rapid deactivation of the active catalyst [10, 23, 42]. The thermodynamics of the process are such that reaction conditions that promote coking are difficult to avoid. Therefore, operating conditions that minimize coke without significantly changing the yield of the products are chosen. One of the most common ways of avoiding coke formation is to increase the steam-to-carbon or CO\textsubscript{2}-to-carbon ratios in order to avoid methane cracking by providing excess reactants for the reforming reactions and to make reactions 2.5 and 2.7 go in the reverse direction. Eguchi et al. [43] have developed carbon limit diagrams which relate the propensity of the catalyst to coke to the aforementioned ratios. The ternary phase diagram has been presented in Figure 2.3. The success of these coke controlling measures is evident given the widespread industrial implementation of steam-methane reforming. However, it is expensive to produce excess high temperature steam and measures that can reduce coke formation will have significant economic advantage on the methane reforming process.

As in other catalytic reforming processes, the problem of carbon formation also arises in internally reforming SOFCs. The high steam-to-carbon ratios used in industrial steam-methane reforming to avoid coking is not an attractive option in a SOFC because it lowers
the electrical efficiency of the fuel cell by steam dilution of the fuel [33].

### 2.6 Gasification of Coke

The term “coke” is a collective description of the different kinds of carbon deposits formed on the catalyst surface. These include: pyrolytic carbon, encapsulating films of carbon, and whisker-like nanowires of carbon [44]. Figure 2.4 shows images of the three types of carbon deposits normally encountered. In the presence of excess steam or CO$_2$, gasification of coke and its intermediates is possible by the reverse of reactions 2.5, 2.7, and:

\[
C + 2 \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 2 \text{H}_2
\]  

(2.8)

However, the rate of these gasifying reactions tend to be much slower than those responsible for the deposition of coke [45, 46]. Therefore, it is important to realize that coking
is a process of accumulation, because catalyst coking is dictated by the balance between simultaneously occurring processes that lead to the formation and the removal of coke.

Coke formation on nickel surfaces has been studied extensively, and it is believed that hydrocarbons dissociate to produce species of highly reactive monatomic carbon [47]. This monatomic form of carbon can be gasified easily, however, when an excess of the species is formed, gasification is slow and polymerization occurs. The polymerized carbon species is much less reactive and its gasification is much slower [45]. The polymerized carbon species can then accumulate on the surface or dissolve in the nickel. This can cause the catalyst particles to be lifted out of their sites.

![Figure 2.4: Electron microscopy (TEM) images of pyrolytic carbon on a MgAl₂O₄ carrier (A), encapsulating carbon (B), and whisker carbon (C) on Ni/MgAl₂O₄ reforming catalysts. Reprinted from [25].](image)

Steam reforming of methane also involves the catalyst support and not just nickel. The catalyst support has a major role to play in providing thermal stability to the catalyst pellet and in assisting coke removal from the active catalyst. Catalyst supports are chosen with this in mind [48].

### 2.7 Minimizing Coke Formation

Catalyst that are generally more resistant to coking exist. However, these catalysts are generally made up of noble metals (cobalt, rhodium, etc.), and, despite the fact that carbon formation is less likely over noble metals, the lower cost of nickel drives its use [42].
The choice of catalyst support and the size of the nickel catalyst crystals have a significant effect on the fouling of the catalyst surface by carbon formation during steam methane reforming [37]. The nickel particle size is an important factor for the activity of the steam reforming catalysts. It is easily understood that smaller particles lead to increased specific surface area for catalyzing the reactions and thus improve the activity of the catalyst. Since smaller nickel crystals have more active sites on the surface than larger crystals, the frequency of carbon deposition (turnover frequency) is lower, i.e. the rate of carbon deposition is slower [49]. Hence, smaller nickel particles are more resistant to deactivation by coke formation. It is understood that the carbon formation reactions are sensitive to the structure of the nickel catalyst particles, and the reactions are not able to proceed when the crystals fall below a threshold in size [49]. Consequently, larger nickel particles were found to have a higher carbon deposition rate during the steam reforming of butane [50]. The size of the nickel crystals also had an influence on the ability of initiation or nucleation of carbon nanofibers during methane reforming; it was more difficult on smaller nickel crystals. [51].

Sulfur is a known poison for nickel catalysts and sulfur-poisoned nickel catalysts have essentially no activity below 700 °C [52, 53]. Interestingly, however, studies have shown that sulfur retards the rate of carbon formation more than the rate of the steam-methane reforming reactions [16]. Therefore, small amounts of sulfur on the catalyst surface could be used as a retardant to carbon formation at the expense of a small level of catalyst poisoning.

Boron doping has been found to improve the stability of nickel catalysts during steam-methane reforming by Xu et al. [14]. Density functional theory (DFT) calculations show that boron and carbon exhibit similar chemisorption preferences on a Ni catalyst and, therefore, boron can be used to reduce nucleation sites of carbon on the catalyst surface. Xu et al. verified their theoretical predictions by observing carbon formation during steam-methane reforming on 15 wt.% Ni/Al₂O₃ catalysts promoted with 0.5 and 1 wt.% boron. Using electron microscopy they were able to determine that 1.0 wt% boron reduces the amount of deposited carbon by 80%.
As stated earlier, the choice of the catalyst support is also an important factor for coking in methane reforming applications. The most common catalyst support is alumina [52]. It is generally accepted that the addition of alkali earth metal oxides to the Al$_2$O$_3$ support can improve the catalyst’s resistance to coking. Basic oxides used as support material also improve coking resistance. This positive effect is understood to result from the enhancement in steam adsorption, in the oxidation rate of CH$_x$ fragments adsorbed on metallic nickel and/or the reduction of methane activation and dissociation [13, 54]. Takehira et al. reported that perovskite-type oxides such as SrTiO$_3$, CaTiO$_3$, BaTiO$_3$ that contain a small amount of nickel in the titanium sites show high catalytic activities with high resistance to coking in both partial oxidation of methane and dry reforming of methane applications [55, 56, 57, 36]. Urasaki et al. also found that the perovskite supported catalyst Ni/LaAlO$_3$ showed high methane conversion stability for over 24 hours, whereas the conventional Ni/Al$_2$O$_3$ catalyst was deactivated due to carbon deposition [13]. The lattice oxygen in the perovskites promotes the oxidation of CH$_x$ fragments and hinders the production of inactive carbon species.
The sensors designed by Wheeler et al. were used as the starting point of the study. These sensors utilized a Wheatstone bridge that changed its output voltage when carbon deposits formed on the surface of the sensor. Two of the four bridge elements were made of SLT, and the other two were made of a non-percolating mix of nickel and YSZ. The Ni-YSZ elements were similar in nature to catalyst pellets used in fuel reforming applications, but had a much lower concentration of nickel. In the Ni-YSZ cermet elements neighboring Ni particles were not able to create conduction paths for electrons to travel through, because the concentration of nickel was below its percolation limit. Sanyal et al.’s work was utilized to understand the percolation limit of nickel [20]. The study showed that a Ni-YSZ cermet with 20% Ni by volume has a 0% probability of forming conduction pathways. However, a 30% nickel cermet has a 40% probability of forming conduction pathways. Therefore, carefully choosing a concentration of nickel below its percolation limit ensures a low electrical conductivity in the Ni-YSZ elements. However, as carbon deposits began to appear on the surface of the active Ni catalyst particles, they began forming connections and the electrical resistance of the Ni-YSZ elements decreased. This led to a strong change in the output voltage of the Wheatstone bridge, which was used as the sensor signal.

3.1 Overview of the Sensor Architecture

The sensor architecture was changed significantly from Wheeler et al.’s study to reduce unwanted gas-phase responses. After cold pressing partially stabilized zirconia into a green disc, a Fujifilm Dimatix DMP-2800 printer was used to print the Wheatstone bridge pattern onto the disc using inks containing ceramic powders in suspension. The half-bridge circuit consisted of two elements made up of YSZ and two others made up of a non-percolating mix of NiO-YSZ, which would later be reduced using hydrogen to Ni-YSZ elements. Electrical
connections between the bridge elements and from the Wheatstone bridge to the voltage source and voltmeter were made using a conductive silver paste that was applied using a vinyl stencil. Figure 3.1 illustrates the Wheatstone bridge used in the sensor and a sample sensor is also shown.

![Diagram of Wheatstone bridge](image)

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

Figure 3.1: The half-bridge circuit that serves as the fundamental working mechanism of the sensor. All four elements of the Wheatstone bridge contain YSZ. Inset: A typical sensor has a diameter 21.5 mm and is 2.8 mm thick.

As was discovered during the course of experimentation, the dominant form of carbon deposits in the oxidizing environments prevalent in methane reforming systems is different from the reducing environment under which Wheeler et al.’s sensors were tested (see Figure 1.1) [4, 58]. In the reforming conditions investigated, very few nanowires of carbon formed on the nickel particles; instead, most of the carbon took the form of films encapsulating the nickel particles. Firstly, carbon nanowire formation rate is a strong function of hydrocarbon structure; the rate decreases in the order: acetylenes (alkynes), olefins (alkenes), and paraffins (alkanes). Wheeler et al. used ethylene (an alkene) as the coke precursor, whereas methane (an alkane) was used in the tests described in this thesis. Therefore, fewer nanowires of carbon are expected. Furthermore, in the presence of steam, the solubility and/or mobility of
monatomic carbon in the catalyst metal particles is decreased [4]. Since the nucleation/initiation of carbon nanowires on nickel particles requires some carbon to be absorbed into the particles, fewer nanowires of carbon form when steam is present.

Since the carbon deposits complete the circuit in the non-percolating nickel, it was necessary to increase the NiO loading in the NiO-YSZ ink to decrease the proximity of the nickel particles and to ensure that the carbon films were able to significantly change the electrical conductivity of the Ni-YSZ bridge elements before they covered the entire surface of nickel particles and stopped growing. The nickel loading was increased by 25%, i.e. the wt.% of NiO in the NiO-YSZ ink was increased from 3.8% used by Wheeler et al. to 4.7%. The effect of increasing the nickel loading by 25% on the sensor response is shown in Figure 3.2. Sensors printed using NiO-YSZ ink with an even greater nickel loading (5.7 %) did not significantly improve coking response, while increasingly being at risk of forming percolating layers of nickel (refer to the “Results” section). Sensors with 4.7 wt.% NiO in the NiO-YSZ ink corresponds to 18 vol.% Ni in the sensor if all the NiO is assumed to be reduced to Ni and no pore-former is added. The addition of pore former further decreases the volume fraction of Ni. Therefore, the ink formulation resulted in a non-percolating Ni-YSZ cermet. Additional details of the ink formulation is provided later.

Figure 3.3 illustrates the sensor appearance at different stages of testing. Electrochemical blackening of YSZ gives all tested sensors a dark appearance as seen in Figure 3.3(b). To verify this, energy-dispersive X-ray spectroscopy was conducted on parts of the coked sensor surface not containing Ni; and, unsurprisingly, no traces of carbon were found in those regions. In fact, the sensor shown in the inset of Figure 3.1 is a coked sensor that had no electrical connections made to it. Consequently, the appearance of this sensor is very different to that in Figure 3.3(b). Figure 3.4 summarizes the design changes made to the sensor.
Figure 3.2: Effect of increasing nickel loading. Sensor performance in steam reforming tests is greatly improved by increasing the nickel loading by increasing the NiO wt.% in the NiO-YSZ ink from 3.8% to 4.7%.

Figure 3.3: Sensors at different stages of experimentation. (a) A printed and sintered sensor. Some contamination from the sintering process is visible. (b) A sensor with the bridge elements connected by a thin layer of silver paste. (c) A coked sensor with the silver connections removed. Note that the electrochemical-blackening of YSZ changes the appearance of the entire sensor surface [59].
3.2 The Problem of Gas-phase Response

The first step in characterizing the sensor response under steam methane reforming conditions was to test them in a dry (CO$_2$) methane reforming environment. This was an important intermediate step because conducting dry reforming tests was possible without significant alterations to the existing test stand architecture. While the sensors developed by Wheeler et al. were successful in yielding a strong electrical response to coking conditions in reducing environments, they were especially prone to large unwanted gas-phase responses when exposed to oxidizing conditions. In particular, after the printed and sintered sensors were reduced under forming gas at 600 °C, they produced a strong electrical signal when the gas environment was changed to CO$_2$. Essentially, any significant change in the partial pressure of oxygen resulted in a strong gas-phase response. Similar behavior was also observed under flows of N$_2$ and CH$_4$. 
In similar in-situ coke deposit monitoring experiments, Müller et al. noted that the gas composition surrounding a catalyst pellet significantly changed the impedance of the pellet, as measured by impedance spectroscopy [60]. In Muller et al.’s study, the impedance change due to changing gas environment was ignored because the change due to coking was much larger — by several orders of magnitude — in the coke loadings of interest (>2 wt.%). However, at low coke loadings, the gas-phase signal was significant.

In the experiments for this project the gas-phase response far exceeded the response from coking of the nickel surface, meaning that an automated computer program analyzing the signal would not be able to distinguish a response due to coking from that due to a change in the gas environment. It should be noted that the sensor catalyst described here is much smaller than a 0.5 cm × 0.5 cm cylindrical pellet used by Müller et al. Hence, the coking signal may not be as large. And in the early stages of coking, the coke load is also very low.

The electrical conductivities of YSZ and SLT exhibit strong dependence on the partial pressure of oxygen (pO$_2$) [61, 62, 63]. Figure 3.5 and Figure 3.6 show the electrical conductivity of YSZ and SLT, respectively. While the electrical conductivity of YSZ increases with increasing pO$_2$, the reverse trend is exhibited by SLT. And, since the electrical properties of YSZ and SLT changed differently for the same pO$_2$ change, the Wheatstone bridge output voltage showed a large response [64]. Therefore, gas-phase response due to changing conductivity of the Wheatstone bridge elements was difficult to avoid entirely. However, when SLT was replaced by YSZ for the non-catalytic elements of the bridge circuit, the gas-phase response was diminished by almost ten-fold (see Figure 3.7). The principle behind this observed drop is that as the sensor environment changes, the electrical conductivity of the YSZ changes similarly across all four element of the Wheatstone bridge circuit. The result is that the bridge output voltage changes less under this scenario then when the electrical conductivities of the different elements (YSZ and SLT) change by different amounts [64]. Note that although the electrical properties of YSZ and SLT are temperature dependent, thermal response from the sensor was unlikely because the inlet gas flows were fully heated.
to the target temperature before they were incident on the sensor surface. The gas flow rates are low enough to allow for laminar flow inside the gas delivery tube and the tube itself is long enough that under a constant tube wall temperature assumption, the corresponding heat transfer coefficient derived from the Nusselt number [65] is sufficient to heat the inlet gases to the temperature of the sensor surface.

Figure 3.5: Electrical conductivity of YSZ sintered in air at 1450 °C and 1600 °C. Although the effect of oxygen partial pressure is not directly shown, it can be understood from the effect of increasing the mol % of yttria in YSZ. As the mol % of Y₂O₃ increases, the number of oxygen vacancies in YSZ also increases and leads to a decrease in conductivity. As a corollary, increasing pO₂ should decrease the number of oxygen vacancies and increase the conductivity. Reprinted from [61].

3.3 Sensor Manufacture

The microstructure of a sensor is crucial to its performance. The amount and concentration of catalyst on the sensor surface dictates the performance of a given sensor. In order
Figure 3.6: Electrical conductivity at 1000 °C of SLT (La$_x$Sr$_{1-x}$TiO$_3$) sintered in air as a function of oxygen partial pressure (pO$_2$). Reprinted from [62].

Figure 3.7: Comparison of gas-phase sensor response. CO$_2$ flow is turned on at $t = 60$ s, turned off at $t = 150$ s, turned back on at $t = 270$ s, and turned off again at $t = 370$ s. The solid line represents the response observed using Wheeler et al.’s sensor architecture. The newer design shows a ten-fold reduction in the gas-phase response (dashed-line).
to achieve repeatability of sensor signals, it is important to minimize microstructure variation between sensors. Therefore, carefully controlled inkjet printing techniques are utilized to deposit uniform layers of cermet to make a Wheatstone bridge with a precise geometry. Making a sensor is a multi-step process. The sections below describe each step in detail.

3.3.1 Ink Formulation and Preparation

The first step in making a sensor is preparing the inks that will be used to print the Wheatstone bridge elements. The inks are essentially colloidal suspensions of metal oxides and other fine powders. They require several hours to become stable and well-dispersed in the solvent as stirring alone is not sufficient to make a stable suspension. A steric stabilizer that covers the particles with polymers whose chains repel each other is used in the inks. The stabilizer/dispersant ensures that the solid particles stay apart and do not form aggregates due to interaction forces between particles [66]. Aggregates of solid particles can block the printer cartridges. Three different inks are required: a SLT ink, a YSZ ink, and a NiO-YSZ ink. All of the three inks use α-Terpineol as a solvent. α-Terpineol gives the inks the required final viscosity for successful jetting through the printer printhead [67]. SLT (20% strontium) powder was obtained from Fuel Cell Materials, YSZ powder was obtained from Tosoh USA, Inc., and NiO powder was obtained from Novamet Specialty Products Corp. Vale Inco Grade F Black Nickel Oxide powder was used. The NiO powder had a mesh size of approximately 2 microns. Sensors made with smaller nickel oxide particles (<50 nm) did not yield strong responses to coking conditions, as shown in Figure 3.8. In fact, the size of the active nickel particles plays an important role in the rate of coke formation, with smaller particles generally less susceptible to coking [17, 37, 49, 50, 68]. The Vale Inco NiO powder used was near the upper limit for the allowable particle size in the Fujifilm Dimatix printer.

As with the sensors manufactured by Wheeler et al., the work of Faino et al. [67] was used to develop the NiO-YSZ and YSZ ceramic suspension inks. Details of the ink formulation are in Table 3.1. To promote gas transport in the active catalytic elements Esprix MX-150 1.5 μm polymethyl methacrylate (PMMA) particles were used as a pore former in the NiO-YSZ
Figure 3.8: Effect of nickel particle size on sensor response. Sensors were tested in dry-methane reforming coking conditions. Sensors made using NiO-YSZ ink with the larger NiO mesh size gives more than a 5-fold increase in sensor response.

Ink. Solsperse 13940 was used as a dispersant.

Table 3.1: Ink formulations used to print sensors.

<table>
<thead>
<tr>
<th>Material</th>
<th>NiO-YSZ ink (wt.%)</th>
<th>YSZ ink (wt.%)</th>
<th>SLT ink (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Terpineol</td>
<td>72.4</td>
<td>79.0</td>
<td>72.5</td>
</tr>
<tr>
<td>NiO</td>
<td>4.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>YSZ</td>
<td>15.0</td>
<td>15.0</td>
<td>-</td>
</tr>
<tr>
<td>SLT</td>
<td>-</td>
<td>-</td>
<td>27.0</td>
</tr>
<tr>
<td>Solsperse 13940</td>
<td>6.6</td>
<td>5.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Pore Former</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Preparation of the inks is fairly straightforward. The necessary ingredients listed in Table 3.1 are measured and mixed together in a glass vial to make a 10 g batch of ink. To aid in forming a stable suspension, 1/4 inch zirconia milling balls are added to the vial, and the ink containing vial is placed in a ball mill for 24 hours to allow thorough mixing. All inks
should be prepared under a fume hood, and skin contact with any ink or precursor material should be avoided.

### 3.3.2 The Printing Process

To print the desired patterns for the Wheatstone bridge using the Fujifilm Dimatix printer, bitmap images of the pattern must be created. The image editing software GIMP was used to make the print patterns. A black pixel in the bitmap image corresponds to a drop of ink, and white pixels correspond to blank areas. For the bitmap image to be correctly interpreted by the printer, the image should have a 1-bit color depth, i.e. strictly black and white. The resolution of the image should also match the droplet spacing of the printer. Once a bitmap image of the pattern has been made, it can be converted to a usable pattern for the printer using the Dimatix software’s “Import Bitmap” feature. The Dimatix user’s guide provides step-by-step instructions to using the Dimatix software.

The Wheatstone bridge pattern is printed on a 1-inch PSZ (partially stabilized zirconia) disc. A green PSZ disc is made by cold pressing 4.0 g of PSZ powder in a cylindrical die. A force of 5000 lbs is applied to the die for 10 seconds using a programmable hydraulic press. The PSZ powder includes binders that provide the pressed disc sufficient green strength to survive the printing process.

The PSZ disc is placed on the substrate holder of the printer to begin printing. The inks are injected into 1.5 mL capacity cartridges using a syringe. The cartridges are reusable. To use them again, however, the larger of the two sets of security tabs used to link the ink reservoir to the cartridge head must be cut off before the cartridge head is attached to the reservoir. First, ten layers of SLT ink is printed on the entire surface of the disc. At this time, the printer’s substrate holder is maintained at 50 °C to facilitate drying of the ink. Next, eight layers each of YSZ and NiO-YSZ inks are printed on the disc to make the four elements of the Wheatstone bridge. After printing with each ink, the printhead must immediately be cleaned by gently flushing alcohol through the nozzles. This prevents leftover ink in the nozzles from drying up and clogging the printhead.
Multiple sensors can be printed at a time. However, they need to be aligned in a straight line. A plastic alignment tool is used. The tool has a $3 \times 3$ array of slots that match the size of a green PSZ disc. Using the alignment tool, in conjunction with the “Theta Calibration” feature of the printer, up to nine sensors can be printed at a time. The entire process to print a batch of nine sensors, from pressing the discs to completing the print job, takes around 6 hours to complete. The printer is faster along the $x$-axis than the $y$-axis. So if three sensors are required, it is best to place them in a single row for printing.

### 3.3.3 The Sintering Process

Printed sensors are sintered in air. Using a Deltech furnace, the sensors are first heated to 300 °C at 60 °C/hr. They are then held at 300 °C for 3 hours to burn out the binder, dispersant, and pore former. Then, the sensors are heated again to 1450 °C at 240 °C/hr. The sensors remain at 1450 °C for an hour. At this time the bulk of the grain growth takes place. The sintered sensors are cooled to room temperature at a rate no faster than 240 °C/hr. During sintering, it is important to cover the top surface of the sensor with a block of solid alumina. The alumina cover should not touch the sensors. The purpose of the dense alumina cover is to prevent any contamination of the sensor surface during the sintering process. Previously, glassy droplets on the order of 0.1 mm appeared on the sensor surface while they were in the sintering furnace (see Figure 3.9). These contaminants come from other materials sintered in a shared furnace and are likely to affect the performance of the sensors. Covering the printed sensors with a dense, inert ceramic material stops the contamination from appearing.

When using the furnace to sinter a batch of sensors, care should also be taken to place the sensors far from the furnace walls and close to the center. If the sensors are placed too close to the furnace heating elements, bubbles may appear on the sensor surface from rapid heating (see Figure 3.9).

After sintering, the sensors are placed in a reducing furnace and are heated to 600 °C at 4 °C/min while they are exposed to a flow of 10% H$_2$ balanced by N$_2$. The sensors are held
in the reducing furnace at 600 °C for 24 hours in order to reduce the printed NiO to active catalytic Ni. Note that while a certified forming gas mixture may be used, such mixtures typically have a hydrogen concentration of less than 4% by volume, and sensors reduced under a certified forming gas mixture were still visibly green after 24 hours, indicating that not all of the NiO has been reduced. Other researchers in the lab working with similar NiO-YSZ materials for fuel cell anode applications also reported incomplete/slow reduction of NiO when using a certified forming gas mixture. Therefore, a gas mixture with a higher hydrogen content is recommended. Mixing together flows of hydrogen and nitrogen is the easiest way to achieve this. The individual gases also tend to be far less expensive than a certified mixture. However, great care should be taken while operating with pure hydrogen. Hydrogen generally burns with a flame invisible to the naked eye, and a mix of 10% hydrogen in nitrogen is above the flammability limits of hydrogen. Steps should be taken to ensure no leaks are formed at any time during the reduction process.
During testing, the sensor was housed inside a quartz tube placed in a tube furnace, which was used to control the temperature of the test cell. The flanged tube is solid at one end and open at the other. A removable metal flange was affixed to the open end of the quartz tube. The metal flange has holes for: gas inlet and outlet lines, a thermocouple, and a 4-holed alumina tube housing the wire connections to the sensor. The sensor was mounted on the end of a 25 mm Swagelok nut that was connected to the gas inlet lines. Connections to the voltage source and the voltmeter used to deliver and measure the input and output voltages of the Wheatstone bridge were made using platinum wires attached to the conducting silver paste. The test cell is illustrated in Figure 4.1. The input to the bridge circuit of the sensor was a 5 V DC excitation voltage from a Fluke PM 2812 DC power supply, and a Keithley 2420 sourcemeter was used as a voltmeter to measure the voltage output from the sensor. Data acquisition hardware from National instruments and LabVIEW software were used to record the voltage, temperature, and gas-flow data. Electrical connections to the sensor were made using platinum wire. A small section of the wire was bent over the edge of the sensor, like a hook, and additional silver paste was applied to secure the silver wire to the bridge connections on the sensor surface made by applying silver paste through a stencil (see Figure 4.2). The wires wrapped around the edge were electrically insulated from the stainless steel sample holder by mica washers placed between the sensor and the holder assembly. Note that while silver wires were used previously, all wiring was changed to platinum to accommodate steam reforming tests. This is because steam reacts with the silver wires to corrode and eventually break them.

The steam required for steam methane reforming tests was generated using an inline bubbler. A 0.5 SLPM flow of carrier gas ($N_2$) was delivered to the stainless-steel bubbler
containing deionized water which was maintained at 70 °C. The lines carrying the wet gas were heated using rope heaters and maintained at 150 °C. This ensured that all the steam obtained from the bubbler was delivered to the test cell without any condensation inside the
lines. Under the conditions stated above the bubbler was able to deliver 2 g of steam per hour (±10%), as measured by loss of liquid mass in the bubbler over time.

Figure 4.3 illustrates the experimental setup. The gas delivery system was made up of three mass flow controllers: one for the carrier gas for the bubbler (N₂); one for both H₂ and CO₂, separated by valves; and, a third one for CH₄. For the reduction cycle, mass flow controllers 1 and 2 were used to create a mixture of H₂ and N₂. The gas lines bypassed the bubbler during this time. Mass flow controllers 1 and 3 were used for steam-methane reforming tests, and 2 and 3 were used for dry-methane reforming tests. The reforming reactants were delivered to the sensor using an inert alumina tube. The alumina tube is important because stainless steel typically contains nickel which could catalyze the reforming reactions and deplete the reactants before they are incident on the surface of the sensor.

Figure 4.3: Illustration of experimental setup.
Sensor testing began by heating the test cell to 600 °C while exposing the sensor to a mixture of 10% hydrogen balanced by nitrogen. The test cell was left at 600 °C for 24 hours in order to reduce the nickel oxide to nickel. After the reduction cycle was complete, a non-coking mixture of methane and steam (or carbon dioxide for dry reforming tests) was introduced into the test cell (see Table 4.1 and Figure 4.4 for details of the composition). After a stable baseline voltage was established (usually this took several minutes after stopping the flow of the reducing gas mixture and introducing the reactants of the reforming process) coking conditions were produced by increasing the flow of CH$_4$ until the steam-to-carbon (or CO$_2$-to-carbon) ratio was 1:1. The required CH$_4$ flow for steam reforming tests was determined by converting the mass loss rate of the water in the bubbler to a molar flow rate of steam, which is used to determine the required molar flow rate of CH$_4$ for a desired steam-to-carbon ratio. The voltage output from the sensor was monitored carefully during the coking process.

Sensors were regenerated by flowing 2 g/hr of steam (carried by 0.5 SLPM N$_2$) over the coked sensors at 600 °C for 20 hours to remove carbon deposits. After regeneration the sensors were reduced and coking tests were repeated as above.

The gas flow rates used for the tests have been tabulated in Table 4.1. Figure 4.4 shows each reforming gas mixture on a C-H-O ternary phase diagram.

Table 4.1: Gas flow rates used for testing. Points A–D correspond to the points on the ternary phase diagram in Figure 4.4.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Flow Rate (SLPM)</th>
<th>Bubbler</th>
<th>Point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N$_2$</td>
<td>H$_2$</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>Reduction</td>
<td>0.09</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>Steam Reforming</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-coking</td>
<td>0.5</td>
<td>-</td>
<td>0.015</td>
</tr>
<tr>
<td>Coking</td>
<td>0.5</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>Dry Reforming</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-coking</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>Coking</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>Regeneration</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4.4: Reforming gas mixtures on a C-H-O phase diagram. Point A corresponds to a non-coking steam-methane mixture, where the steam-to-carbon ratio is 3:1. Industrial steam-methane reformers typically operate at this ratio (or higher) as carbon deposition can be avoided. Point B corresponds to a steam-to-carbon ratio of 1:1. At 600 °C, B is conducive to carbon deposition on the catalyst surface. Point C corresponds to a safe non-coking mixture of CO\textsubscript{2} and methane at 600 °C. Note that the CO\textsubscript{2}-to-carbon ratio is 20:1. Point D has a CO\textsubscript{2}-to-carbon ratio of 1:1 and lies within the carbon deposition prone region at 600 °C. However, at temperatures >800 °C, point D lies just outside the carbon deposition region. Adapted from [69].
The main results have been categorized and reported in the sections below. Since the main target industry of a functional sensor is steam-methane reforming, a majority of the tests were conducted in conditions replicating steam-methane reforming. In fact, the dry-methane reforming test results reported here were obtained after the sensor performance in steam-methane reforming tests was at a satisfactory level.

About 75% of the sensors exposed to coking conditions found in steam-methane and dry-methane reforming processes demonstrated strong signals to coking stimuli. This number can be as high as 90% if adjusted for sensors that did not work due to erroneous wiring, which often lead to excess noise in the sensor signal. Figure 5.1 shows a couple of instances where coking signals were degraded by poor connections to the sensor. In the working sensors, the response from coke formation was much greater than any gas-phase response, which were usually on the order of tens of millivolts.

Table 5.1 summarizes all the different test results obtained from sensors manufactured using the new design. Of the nineteen sensors tested, fourteen showed strong responses to coking. The coking responses from two sensors were below 100 mV and difficult to distinguish from gas-phase responses. Three other sensors had their response compromised due to poor wiring of the sensor to the electronics.

5.1 Steam Reforming Response

The sensors tested in conditions replicating steam methane reforming showed a strong response to the presence of coking conditions. After introducing a non-coking mixture of reactants into the test cell, the signal was observed for several minutes. A small gas-phase response was observed when steam was first introduced into the test cell. The magnitude of this response, however, never exceed a coking response. Figure 5.2 shows how a gas phase
Table 5.1: Summary of sensor test results. A good coking response is in the range 100–300 mV, a poor response is <100 mV, and an excellent response is >300 mV. Unless otherwise noted, all sensors were printed using 4.7 wt.% of NiO powder in the NiO-YSZ ink.

<table>
<thead>
<tr>
<th>#</th>
<th>Test</th>
<th>Coking Response</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Steam reforming</td>
<td>Excellent</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Steam reforming</td>
<td>Good</td>
<td>5.7 wt.% NiO</td>
</tr>
<tr>
<td>3</td>
<td>Steam reforming</td>
<td>Good</td>
<td>5.7 wt.% NiO</td>
</tr>
<tr>
<td>4</td>
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<td>-</td>
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<td>N/A</td>
<td>Poor wiring</td>
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<tr>
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<tr>
<td>7</td>
<td>Steam reforming</td>
<td>Excellent</td>
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<td>8</td>
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<td>Excellent</td>
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response from steam compares to a coking response of the same sensor. After the sensor signal was stable under a non-coking flow of reactants, the flow rate of methane was increased to form a coking mixture, as determined from a C-H-O phase diagram. The sensor signal was monitored for several minutes under coking conditions until it started to plateau due to saturation of carbon deposits on the sensor surface. Figure 5.3 presents the data from five
Figure 5.1: Examples of signals from poorly wired sensors. Although a trend (coking signal) is clearly discernible, the excess signal fluctuations due to poor wiring undermine the usability of the signal. Some of the fluctuations directly followed external vibrations of the test stand.

different sensors. Most of the sample sensors had signals on the order of 200-300 mV. The trends in the response from the different sensors are almost identical: a steep (fairly linear) initial response, followed by a steady decline in the slope until the sensor surface becomes saturated with carbon and its catalytic activity is largely lost.

The variation in sensor response may be attributed to: (a) the microstructure variations between sensors, either due to subtle changes during the printing process, or external contaminations within the kiln during sintering; and, (b) changes in electrical connections between tests owing to the silver paste connections, which must be made each time by hand. In fact, not all of the sensors reported in Figure 5.3 are from the same manufactured batch. Although they all have the same design, sensors 2 and 3 were printed using 5.7 wt.% NiO in the NiO-YSZ ink (50% increase from Wheeler et al.’s formulation), while the others had 4.7 wt.% NiO. Since the responses were varied and not significantly improved by using 5.7 wt.% NiO, all subsequent sensors were manufactured using 4.7 wt.% NiO in the NiO-YSZ
Sensors 6 and 7 belong to the same batch, but the reason for the large disparity between their responses is not fully understood.

Figure 5.2: Comparison of gas-phase response to coking response. Steam is added to the test cell at $t = 500$ s. A gas-phase response of about 60 mV is observed. After the signal stabilizes, the CH$_4$ flow is increased at $t = 1800$ s to coke the sensor. The coking signal is much greater in magnitude than the gas-phase response.

5.2 Dry Reforming Response

The sensors also exhibited a good response to coking conditions during CO$_2$ reforming of methane (Figure 5.4). The signals exhibit trends similar to the steam reforming responses. However, the variation between signals from different sensors is smaller. The lack of variation could be due to a smaller set of sensors investigated under CO$_2$ reforming tests than under steam reforming tests. Furthermore, all three sensors reported in Figure 5.4 were manufactured in the same batch, which can result in added microstructure uniformity between sensors.
Figure 5.3: Sensor response to coking in a steam reforming environment. At $t = 1000$ s additional CH$_4$ is added to promote coking. The response of sensor 7 has been reduced by a factor of 2 to better accommodate it on the axes.

5.3 Images of the Sensor Surface

Using a field-emission scanning electron microscope (FESEM), the catalytic surfaces of the uncoked and coked sensors were examined. Figure 5.5 and Figure 5.6 show the images obtained from the FESEM of an uncoked and a coked sensor surface, respectively. The image of the coked sensor surface shows nickel particles encapsulated in a film of carbon. The nickel particles were correctly identified and the layer of carbon on them was verified using the energy-dispersive X-ray spectrometer (EDX) attached to the FESEM. The EDX feature can detect elements with large atomic numbers such as nickel at low excitation voltages (around 2 keV), however, larger excitation voltages (>15 keV) are required for detecting carbon, which has an atomic number of 6.

In the uncoked sensor the nickel particles have sharp edges and are polygonal in appearance. The bulk YSZ support for the nickel has more rounded grain structures. The YSZ
Figure 5.4: Sensor response to coking in a CO$_2$ reforming environment. At $t = 1000$ s additional CH$_4$ is added to encourage coking.

particles also tend to grow all around the nickel particles during sintering and hold them firmly in place, instead of pushing the nickel particles out on the surface.

In the coked sample the nickel particles can be seen encapsulated in a cloudy layer of carbon deposits. As stated earlier, this was found to be the dominant mechanism of carbon formation on the catalyst in conditions typical in methane reforming processes. Wheeler et al. found carbon filaments to be the chief mechanism of carbon growth on the catalyst surface in coking conditions produced by reacting ethylene and hydrogen. In Figure 5.6 the carbon deposits grow all around the nickel particles and are able to push neighboring YSZ particles away. This results in more distinct boundaries between the coked nickel particles and the bulk YSZ. Most of the coked particles on the surface do not seem to be firmly held in place by surrounding YSZ particles, unlike the uncoked nickel particles. Figure 5.7 shows a rare instance of a carbon nanowire formed on the catalyst surface. It also shows how carbon deposits fill in the gaps between neighboring nickel particles.
Following the success of sensor regeneration by Wheeler et al., the reusability of the sensors was examined. Coked sensors were regenerated by steam, reduced, and then steam reforming coking tests were performed again. Figure 5.8 shows the responses seen from two regenerated sensors. Generally, the magnitude of a sensor’s coking response decreased after it was regenerated. Upon looking closely at the surface of a regenerated sensor under the FESEM (Figure 5.9), the regeneration process seemed to have decreased the proximity and size of the catalyst particles on the surface of the sensor. In fact there was around a 30-40% decrease in the surface density of nickel particles after regeneration. This number was determined by examining several FESEM images of a sensor surface at 3000× magnification, before and after regeneration. Before regeneration, the average density of coked nickel sites
on the surface was approximately 0.20/µm² (one standard deviation was 10% of the mean). After regeneration the number of nickel sites was reduced to about 0.13/µm² (one standard deviation was 14% of the mean).

The loss of nickel particles from the surface can be explained by the growth of carbon under the nickel particles, which is able to push them out of their sites, move neighboring YSZ particles, and eventually contributes to liberating the nickel particles from the bulk YSZ when the carbon layer is removed by steam regeneration [4]. Therefore with fewer nickel particles and the particles farther apart, a regenerated sensor has a weaker response when exposed to the same coking conditions, because the carbon deposits are not able to change the electrical conductivity of the Ni-YSZ as much as before.

In Figure 5.8 we can see that the coking response from a regenerated sensor can be around 100 mV in the second cycle. Additional cycles are likely to decrease the magnitude of the response further. Coking responses <100 mV will be difficult to distinguish from gas-phase responses. Therefore multiple cycles of the sensor may not be feasible. It is worth noting, however, that the sensors were coked severely (for the better part of an hour) before they were regenerated. Sensors coked for a shorter period of time in the first cycle may accumulate less carbon deposits on the surface, which may lead to an increased retention of nickel particles during regeneration, and may lead to a smaller loss in response in subsequent cycles. To test this hypothesis, a sensor was coked for 10 minutes and then regenerated. The regeneration cycle lasted 10 hours. Figure 5.10 shows the results, which indicate that even just after ten minutes of coking in each cycle, the sensor response drops to under 100 mV in the third cycle. This shows that besides carbon removal, prolonged exposure to steam at high temperature may also play a part in the degradation of sensor performance after regeneration cycles.
Figure 5.6: A coked sensor surface shows carbon deposits on nickel particles under a FESEM. The nickel particles are covered with carbon deposits that are cloudy in appearance. Images of the same sensor at two different magnifications are presented.
Figure 5.7: A Carbon nanowire growing on a coked nickel particle. The areas circled in red show how carbon deposits form pathways between neighboring nickel particles.

Figure 5.8: Response from regenerated sensors. The sensors show similar, but smaller, responses to coking in the second cycle.
Figure 5.9: Surface of a regenerated sensor as seen under a FESEM. Images of the same sensor at two different magnifications are presented. Nickel particles appear to have shrunk in size and are generally farther apart compared to a fresh sensor. The particles also appear to sit freely on the surface rather than being closely surrounded by YSZ particles, increasing the likelihood of loss of nickel particles from the surface during the regeneration process. Clusters of very small particles are indicative of spalling of larger nickel particles [4].
Figure 5.10: Sensor response over multiple cycles. In each cycle, the sensor is coked for just 10 minutes. By the third cycle, the sensor response drops below 100 mV.
Building upon existing work on an impedance-based sensor, a novel carbon sensor that can detect the early stages of catalyst coking in methane reforming systems has been developed. The sensor response has been characterized in simulated coking conditions typical to steam-methane and dry-methane reforming. Undesired gas-phase responses from the sensor were reduced by making major changes to the sensor design. This improves the feasibility of using the sensor signal to control the feed in a methane reformer to avoid catalyst coking. Using FESEM imaging, the nature of the carbon deposits on the active nickel surface was understood. Reusability of the sensor was investigated by regenerating coked sensors using steam. Regeneration of the sensor leads to a large degradation in the sensor performance. The coking signal decreases almost by a factor of 2 after each regeneration cycle.

While the sensor signal may not be feasible for multiple cycles, the relatively low cost of the manufacturing materials can attract industrial implementation, even if a sensor has to be replaced after being saturated by coke. Currently, the materials cost for a sensor is under $1. For use in an industrial-scale reformer, an array of sensors can be placed along the length of the reformer tube. The signal from each sensor can provide information about the presence of gas mixtures conducive to fouling of the catalyst by carbon deposits at each location. Since the composition and temperature will vary along the reformer tube (as will the propensity to coke the catalyst) it is important to use an array of sensors to monitor local coking conditions.
6.1 Future Work

To make the sensor into a marketable device, some additional refinements and studies are required.

The electrical connections of the sensor has significant room for improvement. The sensor holder can be redesigned to incorporate connection ports for the sensor, which can allow for easily connecting the sensor to the electrical hardware. A sensor with improved connectivity, where the electrical connections do not need to be made by hand each time, can be marketed as a plug-and-play type device.

Since the nickel particles are the limiting factor in the performance of the sensor after regeneration, it can be worthwhile to investigate more robust noble catalyst metals which can withstand multiple regeneration cycles. However, the rate of carbon deposition on sensors made with noble catalysts may vary significantly from sensors made with nickel catalyst. Consequently, the sensor signal may be different and not as effective in detecting the early stages of catalyst coking.

To better understand and use the sensor signal, a study to find a direct correlation between the carbon deposition rate and the change in electrical conductivity of the Ni-YSZ Wheatstone bridge element will be helpful. Although the bridge output voltage changes with carbon formation on the surface, it is unclear how/if this voltage change information can be used to accurately determine a quantitative change in the electrical conductivity of the sensor. An electrochemical impedance spectroscopy analysis of the sensor could shed light onto this issue by measuring the electrical impedance of the sensor over time.

A temperature varying study of the sensor performance may be helpful. All of the current tests were conducted at 600 °C. This is at the low end of the methane reformer operating temperature spectrum. It is not known how the sensor signal may vary with changing temperature. Coking rate is expected to increase with increasing temperature. While it is not a difficult parametric study to perform, operating the sensor testing cell at higher temperatures will requires major alterations to the test-stand setup. Knowledge of
the temperature relationship of the sensor signal will be useful for implementation in an industrial reformer, where the temperature is not constant and varies along the length of the reformer tube [11].

Similarly, testing the sensor at elevated pressures is important. All tests to date were performed at ambient temperature. Methane reformers typically operate in the 5–15 atm pressure range. Therefore, testing at elevated pressures will show how the sensor behaves in more realistic conditions. Pressurizing the test cell will also require significant modifications to the setup.

The sensor manufacturing process may have room for refinement in order to decrease the microstructure variation between sensors. Since the microstructure is directly related to the sensor signal, uniformity in microstructure may decrease signal variance between sensors exposed to the same coking conditions. With reduced signal variation, a group of sensors may be used synchronously in an industrial reformer to monitor both global and local coking of the catalyst pellets.

As discussed earlier, the catalyst support plays an important role in the formation of carbon deposits on the active catalyst. The support material for the catalyst in the sensor is partially-stabilized zirconia. While this is certainly consistent with the support material used in internally methane reforming solid oxide fuel cells, catalyst pellets in industrial steam-methane reformers use altogether different support materials (typically alumina). An investigation into the feasibility and effect of replacing alumina as the sensor support can be insightful. The rate of carbon deposition, and therefore the coking signal, could be different for different catalyst supports.

The effectiveness of the sensor in saving an industrial catalyst may be examined by placing a catalyst sample in the test cell. Electron microscopy and/or thermogravimetric analysis can then be conducted on the catalyst to determine how much coking occurs in the time required for the sensor to produce a signal and then for the signal to be interpreted correctly by a feedstock controlling computer.
The gas-phase response from the sensor may be reduced further by using a metallic conductor, instead of YSZ, for the non-catalytic half of the Wheatstone bridge circuit. A metallic conductor is less likely to have pO$_2$ dependent electrical conductivity. Research is required to identify possible non-catalytic metallic alternatives to YSZ. If the electrical conductivity of the non-catalytic metal is too high compared to the Ni-YSZ cermet, coking of the nickel particles may not produce a strong electrical signal. Knowledge of the electrical properties of the Ni-YSZ elements will be needed to find a non-catalytic metal or cermet with similar properties that can be printed on the sensor surface.
REFERENCES CITED


