Investigation and development of electro catalysts for Solid Oxide Fuel Cells

Dissertation

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ABSTRACT

Solid Oxide Fuels Cells (SOFCs) have tremendous potential as efficient and clean energy conversion devices. They are the most desirable fuel cells for stationary power generation and as auxiliary power sources in transport applications. The fuel flexibility and higher efficiency of the SOFC make it a favorable choice over conventional combustion systems. However, there are some major roadblocks to the effective commercialization of SOFC technology. High operating temperatures are required due to low activity of the cathode catalysts, thus dictating the use of more expensive materials for the SOFC components as well as balance of plant. Moreover, the state-of-the-art Nickel – Yttria Stabilized Zirconia (Ni-YSZ) cermet anode catalysts are extremely susceptible to poisoning by sulfur in the fuel, as well as coking on operation with carbonaceous fuels. Ni also tends to sinter at elevated temperatures. Since these fuel cells are envisioned to be used with Coal and Natural Gas as fuels, stable and active anode catalysts are required.

There is a need for significant work in developing and testing new catalyst formulations for both electrodes. The cathode reaction is the reduction of gas phase oxygen to form oxide ions that are then transported through the electrolyte to the anode. At the cathode, the drive is to develop perovskite oxide materials which are capable of conducting and activating oxygen at lower temperatures.
and are more active than the state of the art Lanthanum Manganite based catalysts. The current research focused on developing new formulations based on doping of Lanthanum Ferrites and exploring their properties and their activity and performance as SOFC cathodes. The effect of varying the dopant levels on the physiochemical properties as well oxygen mobility and oxygen content in the samples is explored. The effect of substitution of the La ions with Sr on the A-site is studied in detail and the oxygen activation and transport properties are explored as a function of Sr content. Methane oxidation is used as a model reaction to study oxygen activation energies over the materials. X-ray Photoelectron Spectroscopy and Mössbauer Spectroscopy are used to study the surface and bulk properties. Additional doping with aliovalent metals such as Zn, Cu and Ni on the B-site is studied and the surface and bulk properties are examined using X-ray Diffraction (XRD), Thermogravimetric analysis (TGA), X-Ray Absorption Fine Structure (XAFS) techniques and using methanol as a probe molecule. Further in-sight into oxygen activation properties is obtained by CO₂ Temperature-Programmed Oxidation (TPO) and methane oxidation reactions.

On the anode side, the emphasis is in exploring the nature and mechanism of deactivation of the state of the art Nickel-Yttria stabilized Zirconia (Ni-YSZ) catalysts. The effect of water in sulfur poisoning on the catalyst is examined through steady-state reaction testing as well as bulk and surface characterization using XAFS studies and temperature programmed desorption (TPD) experiments. Based on these results, new formulations are explored and
tested for their activity for the various anode reactions as well as the tolerance to sulfur poisoning and coking. The new catalyst development is carried out in a two pronged approach. Transition metal based bi-metallic catalysts are explored. Simultaneously, perovskite oxide materials are also tested for their catalytic activity and performance as SOFC anodes. Coking and sulfur tolerance studies are performed and characterization is performed using XPS and TPD studies.
DEDICATION

To Appa and Amma
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FIELDS OF STUDY

Major Field: Chemical Engineering

Area of Interest: Heterogeneous Catalysis
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CHAPTER 1. Introduction

The need for the production of energy in a clean and efficient manner and demands for newer alternative technologies and fuels haves been increasing over the past decade. Dwindling fossil fuel resources, increased awareness about emission control and climate change and the growing demand for energy globally, have driven a lot of research in the search for new technologies, cleaner processes and renewable energy sources. Fuel cells are likely to play an important role in this new energy economy. The promise of higher efficiencies and much lower emissions make them an attractive proposition.

Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy. Since they don’t operate on a thermal cycle, their efficiencies are not dictated by the theoretical Carnot cycle efficiency. Moreover, with the direct conversion into electricity, energy losses due to intermediate steps, when compared to the typical power plant or combustion engines, are also avoided. Thus efficiencies higher than the state of the art combustion engines and power generators can be achieved. The efficiency of a fuel cell depends on power density of operation, or the amount of current drawn from it.

Several types of fuel cells operating over a wide range of temperatures and fuels exist. Fuel cells are classified on the basis of the electrolyte used. The
popular types of fuel cells include Polymer Electrolyte Membrane fuel cells (PEM), Alkaline Fuel Cell, Solid Oxide Fuel Cell and Molten Carbonate Fuel Cells. A Solid Oxide Fuel Cell (SOFC) therefore is thus named as it has a solid ceramic oxide material as the electrolyte. SOFCs are the most desirable fuel cells for stationary power generation and as auxiliary power sources in transport applications. The fuel flexibility and high efficiency of an SOFC make it a favorable choice. The SOFC conventionally operates between 800-1000°C. The high operating temperatures of SOFCs enable co-generation applications where the heat released by the exothermic reactions can be utilized usefully. This heat can also be used for the internal reforming of the fuel at the anode and thus practically any hydrocarbon can be used as fuel in a SOFC. Operating directly on hydrocarbon fuels improves overall efficiency. Moreover, overall system design becomes simpler and less expensive. The potential of such internally reforming SOFCs is tremendous. They can be used for a variety of applications including small-scale, remote co-generation purposes, uninterrupted power generation in hospitals as well as eventual incorporation into large-scale distributed power generation. Fuel flexibility and ability to process CO and most hydrocarbons make the SOFCs more efficient in principle than other fuel cell systems. Also the high temperature heat generated make them especially suited for combine heat and power generation systems ranging from applications with 1kW to 100Mw systems. Fuel flexibility also makes SOFCs more suited for stand alone remote applications with bottled fuel/natural gas supplies.
In an SOFC, electrochemical reaction taking place at the cathode is the reduction of oxygen to oxide ions.

\[ O_2 + 2e^- \rightarrow O^{2-} \]  

Reaction 1

The oxide ions are then transported across the electrolyte to the electrolyte-anode interface. The reaction occurring at the SOFC anode is the oxidation of the fuel arriving at the anode. The fuel at the anode is usually hydrogen, syngas, or hydrocarbons in the case of Direct Hydrocarbon Fuel Cells. The key electrochemical reactions taking place at the anode are shown in Reactions 2 and 3. A brief schematic of the SOFC operation is shown in Figure 1.

\[ CO + O^{2-} \rightarrow CO_2 + 2e^- \]  

Reaction 2

\[ H_2 + O^{2-} \rightarrow H_2O + 2e^- \]  

Reaction 3

In addition to the electrochemical reactions discussed above, chemical reactions such as steam-reforming (Reaction 4) and water-gas shift (Reaction 5) become important to convert the hydrocarbon fuel to H₂ streams which are more easily oxidized [1]. Other possible reactions include the direct oxidation of hydrocarbons (Reaction 6) as well as dry reforming with CO₂ (Reaction 7).

\[ CH_4 + H_2O \rightarrow CO + 3H_2 \]  

Reaction 4

\[ CO + H_2O \rightarrow CO_2 + H_2 \]  

Reaction 5

\[ CH_4 + O_2 \rightarrow CO_2 + 2H_2 \]  

Reaction 6
Since the oxide ions are the species transported through the electrolyte, a SOFC has the potential of operating on any combustible fuel[2]. The elevated operating temperature of SOFCs along with the ability to utilize CO as a fuel enables the operation of these fuel cells directly on hydrocarbon fuels. The hydrocarbons are first catalytically converted to CO and H\textsubscript{2} and then electrochemical oxidation takes place[3]. Alternately, direct electrochemical oxidation of the hydrocarbons is possible [2]. The possibility of directly oxidizing
the fuel without an oxidant or steam further simplifies system design and also reduces operation costs. Development of anode materials that are capable of oxidizing a variety of hydrocarbons at SOFC operating temperatures remains a challenge[2]. The ability to reform hydrocarbons significantly reduces losses due to external reforming systems as well as simplifies overall system design and construction. The relative abundance of natural gas makes it a favorable fuel choice. There have been promising results with SOFCs operating on renewable fuels such as waste biogas and landfill gas[4] . Also, there is significant interest in the use of gasified coal as fuel in a SOFC. There have been many studies investigating the catalytic activity of the anode materials for the steam reforming of methane and higher hydrocarbons [5, 6]. With the capability of operating on CO₂-rich fuels such as biogas, the dry reforming of hydrocarbons is also an option available[7].

The major problem with directly operating on hydrocarbons is the propensity towards carbon formation via cracking over the catalyst surface. Moreover the presence of sulfurous compounds in natural gas as well as coal derived hydrocarbons leads to poisoning of the existent anode materials.

The existent technology in SOFCs is not cost effective and there are several inherent problems associated with the cathode and anode catalyst materials. The state of the art SOFC uses an yttria-stabilized zirconia (YSZ) electrolyte, with a strontium-doped lanthanum manganite (LSM) cathode and a mixed nickel/YSZ cermet anode. Slow cathode kinetics enforces higher operating temperatures which in turn result in material selection issues and high costs. To
live up to the promise of complete fuel flexibility, more robust anode catalysts are to be developed. The Ni/YSZ cermet currently used has coking and sulfur tolerance issues. Moreover Ni sinters at high temperatures during prolonged high temperature operations leading to long term stability issues. Sulfur poisoning and coking has always been the Achilles’ heel of fuel reforming catalysts. Modifying the existent Ni catalysts or developing new catalysts that can overcome these issues is one of the keys to developing realistic Direct Hydrocarbon based SOFCs.

The focus of this thesis has been to develop new formulations with improved performance as well developing a better understanding of the structure-property relationships in these materials in order to be able to develop optimized formulations with the maximum activity as well as stability. On the cathode side the focus has been to modify and develop mixed-conducting oxides which can activate and transport oxygen at much lower temperatures. At the anode, the focus has been to study the deactivation of the Ni-YSZ anodes and the understanding of the interactions of sulfur with the catalyst surface. Perovskite based oxide materials are also studied as potential sulfur and coke resistant anode catalysts.
CHAPTER 2. LITERATURE REVIEW

The initial conception of SOFC technology took place with the discovery of solid oxide electrolytes by Nernst in 1899. The early versions used glass, porcelain and other metal oxides and ceramic solids as electrolytes. In the 1930s and 40s the mechanism of oxygen vacancies and anionic conductivity was discovered and Yttria-Stabilized Zirconia was established as a SOFC electrolyte. However, the high temperatures of operation as well as the harsh reducing conditions at the anode hindered the early development of the technology. With the advances in the ceramic production and processing technology as well as a renewed interest in fuel cells since the 1960s, there has been a resurgence in SOFC research and the materials development has been a primary focus since then [3].

SOFCs operate at high temperatures, between 800-1000°C and hence there are very stringent requirements and limitations on the materials that could be used as electrodes. The basic components of a SOFC include the cathode electrode where the oxygen reduction reaction takes place, the anode which is the fuel electrode, and an electrolyte material conducting oxide ions from the cathode to the anode where fuel oxidation takes place. Due to the high operating temperatures, the materials cost for the balance of the system such as the
interconnects, sealants and manifolding materials as well as fabrication costs are very high. There is a strong research interest thus, in lowering the operating temperature of the SOFCs to develop intermediate temperature SOFCs (IT-SOFC) in order to solve the materials cost and durability issues.

2.1 SOFC cathode

2.1.1 Requirements of an SOFC cathode

The cathode reaction in an SOFC is the activation and reduction of oxygen. Currently, the operating temperatures of the SOFC are dictated by the activity of the cathode and electrolyte materials. The cathode catalyst, apart from having very good activity for oxygen reduction, should also be stable in an oxidizing environment. It must also have high electronic conductivity. Use of precious metals as cathodes is precluded by cost. Thus oxide materials with sufficient electronic conductivity are the most commonly researched materials for SOFC cathodes. The choice of material is also limited by the Thermal Expansion coefficient and compatibility with the electrolyte, which is usually yttrium-stabilized zirconia (YSZ). Other oxides such as Scandia-stabilized zirconia, samaria-doped ceria (SDC) and gadolinia-doped ceria (GDC) are also studied as electrolytes for their higher ionic conductivities at lower temperatures. Thermal mismatch with the electrolyte could cause cracking and mechanical disintegration of the cell during operation at high temperature. Chemical compatibility with the electrolyte is also another important factor to consider. Formation of insulating phases by reaction of electrode materials with the zirconia-based electrolyte is known to cause performance losses in SOFCs [3].
At elevated temperatures of operation, the above restrictions limit the choice of cathode materials to precious metals or electron conducting oxide materials [3]. While precious metal cathodes such as Pt, Ag and Au have been studied before, they are undesirable due to their high costs [8, 9]. The most popularly studied class of oxide materials as cathode materials are perovskite oxides of the general form ABO₃.

2.1.2 Mixed conducting-perovskite cathodes

A perovskite oxide has a general formula ABO₃, wherein the A and B site cations have a total charge of +6. The A-site cation is usually a Lanthanide series or rare earth metal, while the B-site is occupied by a transition metal. Perovskite oxides have been used for several catalytic reactions including total and partial oxidation reactions of hydrocarbons and volatile organics, photo-catalysis, and environmental applications such as SO₂ removal. They are also widely studied for their use in oxygen sensors and oxygen separation membranes where their anionic conductivity is utilized to achieve high purity separations [10, 11]. The anionic conductivity as well as electronic conductivity of these oxide materials makes them a favorable choice as SOFC cathodes as well.

2.1.2.a Lanthanum Manganese cathodes

The state of the art SOFC cathode is Strontium doped Lanthanum Manganese (LSM). Sr doping of LaMnO₃ does not create any oxygen vacancies in the material but rather oxidizes the manganese ion causing an increase in electron-hole concentration and hence causes an improved electronic
conductivity [12]. However at high temperatures, solid-phase chemical reactivity problems with YSZ occur, forming insulating phases such as La$_2$Zr$_2$O$_7$, SrZrO$_3$, at the cathode-electrolyte interface. The conductivity of these impurity phases are up to three orders of magnitude lower than YSZ and hence cause severe ohmic losses in the performance of the fuel cell. The polarization losses due to the insulating layers is caused by interfering with the surface diffusion of oxygen as well as the electrochemical oxygen reduction due to limited availability of electronic charge carriers [12]. The nature and the amount of the reactive phases formed are a strong function of Sr dopant concentration and temperature [13].

Moreover, electrical conductivity of LSM based cathodes is also low at lower temperatures (<800°C). Another major limitation is the lack of oxygen ion conductivity [14] and this is also one of the reasons for the poor performance at lower temperatures. It restricts the cathode reaction of oxygen reduction to the surface of the cathode, in the Triple Phase Boundary (TPB) where the gas, catalyst layer and the electrolyte come in contact as shown in Figure 2. Significant efforts have been made in enhancing or replacing the LSM to have mixed conducting oxide materials, so that TPB is extended to the entire cathode area. Oxygen mobility and kinetics of oxygen reduction can be enhanced by the creation of oxygen vacancies [15, 16]. Oxygen vacancies on the catalyst surface serve as sites for the oxygen adsorption and reduction. The oxide ions then hop through the cathode bulk from one vacancy to another to the electrolyte interface. Combined with electronic conduction, the rates of these processes determine the power generation efficiency of a SOFC.
The performance of LSM cathodes can be enhanced by the addition of a secondary ionic conducting layer to the cathode thus extending the electrochemically active area. Doping the perovskite structure on the A-site creates an oxygen non-stoichiometry within the structure and allows the engineering of crystallographic, electronic, and physical parameters. In addition, doping of the B-site with other cations such as Fe, Ni or Co as well as replacing the La with other rare earth elements has been studied [12]. Sr-doped PrMnO$_3$ showed improved performance at lower temperatures and also demonstrated good thermal compatibility with YSZ making it a promising material for IT-SOFCs[17]. It was also found that in general the chemical reactivity with YSZ can
be lowered by the use of smaller lanthanoids at the A-site[18]. A lot of the current research is focused on looking to replace the conventional LSM cathodes completely with other materials such as Strontium-doped Lanthanum Cobaltite and Ferrites (LSC&LSF), in order to improve the cathode kinetics and operating temperatures of the SOFC. These materials, display improved oxygen reduction and conduction capabilities due to their defect structure and presence of oxygen vacancies[10].

2.1.2.b Lanthanum Cobaltite and Ferrite Cathodes

Cobalt based perovskite oxide materials are known for their higher electronic and ionic conductivities [12]. La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ cathodes have an improved electrochemical activity due to higher oxygen diffusivities as well as higher oxygen activation capabilities at lower temperatures[19]. However with high Co loading on the B-site the thermal expansion coefficient (TEC) of the electrode also increases causing a mismatch with the TEC of YSZ and thus causing delamination of the cathode-electrolyte interface as well as thermal cracking of the YSZ [20]. This TEC increase in Co based oxides can be attributed to oxygen vacancy formation as well as spin-state transitions with the Co$^{+3}$ cation [21]. The TEC can be brought down with replacing the A-site La with other cations such as Pr, Nd and Gd [22]. However, the Co based cathodes have other issues also, including increased reactivity with YSZ to form insulating phases, which usually make a diffusion barrier layer necessary [23, 24].
LaFeO$_3$ based perovskite oxides are known to be more stable than the cobaltites, as the Fe$^{3+}$ ion has a more stable electronic configuration and significantly lower reactivity with YSZ. The thermal compatibility of the ferrite cathodes is also close to that of the common YSZ and GDC electrolytes [25]. By doping the A-site with Sr, oxygen vacancies can be incorporated into the lattice and the electrical and ionic conductivities increase and hence the performance of the cathode improves [26]. Additional doping of the B-site with Cu was also found to significantly increase the kinetics for the oxygen reduction reaction[26]. However Cu doping places constraints on the sintering temperature for the electrode fabrication as well as an increased chemical reactivity with the electrolyte material[27]. Changing the A-site dopant did not significantly reduce this reactivity except in the case of La$_{0.8}$Ca$_{0.2}$FeO$_3$ [28].

Incorporating the advantages of both Fe and Co on the B-site, solid solutions of Fe and Co on the B-site have been investigated [29-40]. The La$_{1-x}$Sr$_x$Co$_y$Fe$_{1-y}$O$_{3-δ}$ (LSCF) materials can possess several orders of magnitude higher oxygen diffusion coefficients compared to LSM compositions at the same temperature [34, 41-43]. B-site doping of cobalt into iron boosts the ionic conductivity and concentration of oxygen vacancies in the perovskite allowing for an increase in the kinetics of oxygen activation. Additional doping of the B-site with divalent transition metals such as Cu, Ni have also shown improved properties and performance in preliminary examination [44-50]. The major problem with strontium doped perovskite oxide catalysts remains that, Sr atoms in the lattice are mobile enough to react at the interfaces and form the impurity
phases [51]. Ca and Ba were also studied as the divalent dopant for other applications [52-54] and, in particular Ba, provided a formulation with a suitable thermal expansion coefficient and hence is a candidate for better stability in future prototypes. Materials advances are certainly needed for an optimized balance of performance and stability.

2.1.3 Oxygen reduction reaction mechanism at the cathode

For the development of improved SOFC cathode materials, it is also important to understand the mechanism of the oxygen reduction step at the SOFC cathode. At the cathode, the major limitation is the reduced activity for oxygen reduction reaction and high over potentials caused by slow kinetics at the cathode. In the literature, there is a consensus, that the overall performance limitations are caused by slow oxygen reduction kinetics and mass transfer rates [10, 55-59]. The mechanism of oxygen reduction over mixed conducting oxides proceeds through several steps and there is no one known rate determining step. It is understood that gas-phase O$_2$ needs to be first incorporated into the cathode surface in the form of an electroactive species through chemical steps before it is reduced to oxide ions at the interface. Thus, the performance of a SOFC cathode is simultaneously limited by several factors including adsorption steps and other chemical processes, ambipolar transport and diffusion, interfacial electrochemical kinetics and ionic transport [8]. Thus it is important to optimize the cathode formulation and micro-structure for each of these factors. Performance testing of the cathode yields only a global overall evaluation and
more refined techniques are necessary to discern the contribution of each of these rate limiting steps to the overall performance losses.

Electrochemical Impedance Spectroscopy (EIS) is a popular technique to study SOFC electrodes. Electrochemical Impedance spectroscopy (EIS) is a powerful technique for characterization of real electrochemical systems. The influence of the various governing physical and chemical processes in the system can be distinguished and studied qualitatively using this technique. This technique studies the response of a system to a small amplitude perturbation signal in terms of the relaxation times of the various dynamic processes in the system at different frequencies. EIS is a very popular technique for investigating mechanisms in electrodeposition, electrodissolution as well as in studying batteries and fuel cells.

This technique is particularly useful if the system under consideration is governed by a number of coupled processes. The complex sequences of the various coupled processes such as mass transport, homogenous chemical reaction and electron transfer each influence the output of the electrochemical measurement in a characteristic manner. The difference in the relaxation times of the various processes in the system is the fundamental principle behind this technique. In these systems steady state electrochemical measurements are not useful as such techniques can only identify simple mechanisms with a single rate limiting step. [60-62] . However, the downside to using this technique to study the cathode mechanism is that it is limited to linear responses and thus is unable to capture non-linear kinetic behavior[8]. More recently, non-linear EIS (NLEIS) has
been developed [63]. Based on these studies, further insight into the oxygen reduction mechanism was provided, and it was suggested that oxygen chemisorption or dissociation onto surface vacancies is the rate limiting step [64]. Despite these advances, there is a lot more information about the surface and bulk properties of these perovskite oxides that need to be understood to optimize the catalyst formulation in a scientific manner. From the studies conducted, it is obvious that oxygen vacancies hold a key to the oxygen activation and transport in these oxides.

Previous work in our research group has focused on developing techniques in order to measure and characterize oxygen vacancy generation and characterization of the bulk and surface properties of Sr- and Co-doped LaFeO$_3$. The formation of perovskite structure was monitored both by in-situ XRD and TGA studies. Formulations of the form, La$_{0.6}$Sr$_{0.4}$Co$_{y}$Fe$_{1-y}$O$_{3-δ}$ with varying levels of Co doping in the B-site (y = 0.1, 0.2, and 0.3) were developed. The baseline oxygen content of these materials was determined, and TGA-DSC studies were performed to study the formation of oxygen vacancies in these materials. The oxygen vacancy formation in these materials was found to be a non-linear function of the Co dopant level. A rhombohedral to cubic crystal symmetry transition was found to occur at intermediate Co doping levels in the materials. This transition is favorable, as in a cubic structure, all oxygen sites are equivalent regardless of whether it is occupied or unoccupied. It is important for the oxygen vacancies to be random to help oxygen diffusion in the sample [41].
Methanol was used as a probe molecule to study the surface of these oxide materials. The nature of surface sites present were explored to adsorption-desorption studies with methanol. The amount of Lewis sites and basic sites were determined, and confirmed using IR spectroscopy [65].

The oxygen exchange kinetics was studied in great detail using several characterization tools. The rate at which oxygen is exchanged as well as the oxygen diffusion coefficients were determined by relaxation (TGA-DSC and in-situ XRD) and steady-state isotopic transient kinetic analysis (SSITKA) techniques. Mössbauer Spectroscopy was used to explain the structural transition taking place with changing the Co content [66].

### 2.2 SOFC anode

#### 2.2.1 Requirements of an SOFC anode

The anode side is the fuel side where the oxidation of the fuel by the oxide ions coming from the cathode takes place. The anode environment is thus of reducing nature except at the outlet where the oxidized products come out increasing the chances of catalyst oxidation. Thus the anode material need to stable under the redox conditions at the operating temperatures of the SOFC. High activity for the fuel oxidation reactions as well good electronic conductivity is a requisite. Additionally, the anode should also be thermally compatible with the electrolyte as any mismatches in the TEC will cause cell disintegration at the high operating temperatures of the SOFC. Moreover, the anode must also have a porous structure, allowing for the gas phase reactants to diffuse to the electrochemically active oxidation sites. The biggest issue with the materials
development as well as fabrication of the anode electrodes is to prevent the loss of porosity and sintering of the materials at the high operating temperatures[3]. Also, with SOFCs operating on carbonaceous fuels, resistance to coking as well as poisoning due to other contaminants such as sulfur is an important requirement.

2.2.2 Anode materials

2.2.2.a Cermet anodes

The current state of the art anode material is a porous Ni-YSZ cermet. The thermal expansion coefficient of Ni is significantly different from that of YSZ thus causing the necessity for a cermet electrode with the Ni mixed with YSZ. Ni provides the catalytic activity and electrical conductivity. The YSZ provides a framework for dispersion of the Ni particles and prevents sintering of the Ni particles. Moreover, the YSZ also brings in ionic conductivity to the anode, thus expanding the triple-phase boundary at the anode side. The threshold for the amount of Ni in the cermet is set by the conductivity requirements as well as the TEC[67]. The Ni-YSZ cermets have been studied extensively as SOFC anodes, and there have been several studies focusing on the optimization of the anode microstructure to achieve low overpotentials and high electrochemical activities[68, 69]. The Ni-YSZ has also been evaluated for the reforming and partial oxidation of hydrocarbons, and Ni shows very good catalytic activity for both reactions[5]. The Ni-YSZ catalysts, while demonstrating excellent activity for the anode reactions also have several inherent problems associated with them. Ni sinters at high temperatures and is also known to show propensity toward
carbon fiber formation [70-72]. As the Ni is also a good catalyst for hydrocarbon cracking, these cermets can be used only in the presence of excess steam which adds to the system cost. The deposited carbon, apart from covering catalytically active Ni sites, could also block the pores of the anode causing further degradation in the cell performance [73]. Also, the Ni cermets are easily poisoned by H₂S concentrations in the ppm range [74-83]. This is a major hurdle for operating on natural gas as fuel. Even 5 ppm H₂S was enough to cause a significant drop in the overall cell voltage and hence SOFC performance [84].

The poisoning effect of H₂S is also temperature dependant. At lower temperatures the poisoning effect of H₂S becomes more and more irreversible [84]. While lowering the operating temperature will offer significant cost and materials benefits, reduced temperatures also increase adsorption of sulfur impurities onto the anode surface. New H₂S cleanup technologies including Selexol® process can lower the inlet H₂S concentration in synthesis gas derived from coal to 10ppm only. Finding ways to mitigate these problems can not only reduce the cost of the fuel cell, but reduce the balance-of-plant requirements for gas cleanup.

To mitigate coking issues while working with carbonaceous fuels, Ni cermets with rare earth-doped ceria (RDC) was studied as an alternate cathode [85]. The Ce⁴⁺/ Ce³⁺ redox couple has good oxidation activity. Moreover, the availability of O²⁻ ions over the ceria surface might enhance oxidation of surface carbon and hence prevent coking on the catalyst. Ni/Gd-doped ceria (GDC) cermet anodes have shown good activity for methane oxidation without
carbon deposition [86, 87]. However, the Ni/GDC has shown chemical reactivity issues with YSZ electrolytes. The GDC reacts with YSZ at high temperatures to form insulating layers with ionic conductivities two orders of magnitude lower than the electrolyte [88]. A possible solution to this issue is replacing the Ni with other metals. To maintain the required electronic conductivity, a large amount of metal is required and this precludes the use of precious metals. Other transition metals such as Fe and Co have similar coking issues [89]. Gorte et al have developed copper based catalysts. Copper unlike Ni does not catalyze the formation of carbon and hence has higher coking tolerance [89]. Also, the mechanism of carbon deposition is different in Cu as compared to metals such as Ni, Fe and Co. On Cu, the carbon is restricted to simple deposition on the surface, which can then be easily scraped off [90]. However, Cu is a poor catalyst for hydrocarbon activation [89]. The anode catalytic activity is improved by addition of Ceria to the Cu/YSZ cermet. Ceria is a very well known redox catalyst [91]. In Cu-Ceria-YSZ cermet anodes, Cu provides only electrical conductivity and almost all the catalytic activity for the oxidation of the fuel is provided by the Ceria [2]. However Cu has a lower melting point than Ni making it suitable for only intermediate temperature SOFCs and this also makes the cermet manufacturing difficult. To improve the catalytic activity of the Cu-impregnated anodes, addition of Pt, Pd and Rh has also been investigated [92]. Rh addition showed a significant improvement in the cell performance with methane as the fuel [91]. The Cu-CeO$_2$ based anodes also showed good
tolerance to sulfur poisoning and showed no degradation in activity with the introduction of H₂S in to the fuel feed[93].

Bi- and tri-metallic anodes alloying Ni with other metals including Cu, Fe and Co have been studied [94, 95] and these have shown initial promise. Sulfur containing materials such as CuFe₂S₄, NiFe₂S₄, WS₂, CuCo₂S₄, and CoS₂ were tested in SOFCs with H₂S as the fuel, but deactivation occurred when long term studies were performed [96].

2.2.2.b Mixed conducting oxide anodes

The use of redox stable metal oxides, as potential SOFC anodes is very promising. Oxides don't form carbon under most conditions [90]. Moreover the increased ionic conductivity of these materials increases the extent of the triple phase boundary (TPB). Also, in the case of oxides the electrode material can be a single component as opposed to cermets, which helps overcome issues such as thermal conductivity mismatches and solid state reactions between the components [2]. With the use of mixed conducting perovskite oxides as anodes, all the SOFC components become ceramic materials, making the fabrication and processing of the cell simple. Ceria and doped ceria are excellent oxidation catalysts and their effectiveness as anode catalysts has been widely studied [86, 91]. However the electrical conductivities of these materials is pretty low which causes poor power densities and cell performance[2]. A functional layer of doped ceria placed between the anode and electrolyte improves performance by expanding the TPB [73].
Oxide materials having the perovskite structure are the most promising anode materials. These oxides have a large number of oxygen vacancies, thus providing high ionic conductivity. Moreover, by introducing transition metals, which exhibit multivalence, into the B site, electronic conductivity can be acquired. The small size of the B-site enables the introduction of transition elements into the oxide lattice[73]. Among the perovskites, the titanates and chromites are most promising [97, 98]. Activity of the titanate materials can be attributed to the presence of a Ti$^{4+}$/Ti$^{3+}$ redox couple that is stable even in the reducing conditions at the anode and can accept electrons from H$_2$ or a hydrocarbon in a chemisorption/dissociation reaction step[85]. La-doped SrTiO$_3$ has shown very good activity as an SOFC anode[7]. Studies with Yttria-doped SrTiO$_3$ have also shown promising results [99, 100]. Doping with Yttria increases the electrical conductivity of the SrTiO$_3$ anodes and hence decreases polarization losses. However, the titanate anodes require very high temperature reduction making co-firing of the anode and cathode difficult as these temperatures would break down the current LSM/LSCF cathodes[99, 101]. SrVO$_3$ while displaying high electronic conductivities, is unstable under more oxidizing conditions[102]. Interestingly, perovskites of the formula La$_x$Sr$_{1-x}$VO$_{3-\delta}$ (LSV) have shown selectivity towards oxidation of H$_2$S even in the presence of H$_2$ [103]. This is a very useful result as a layer of LSV could be used in SOFC anodes to oxidize the sulfurous impurities in the feed gas. Ni-based perovskites have also been studied[6].
There have also been studies on LSCF materials as potential anodes [7, 104]. The biggest problem associated with these oxide anodes is their stability in reducing conditions. LaCrO$_3$ based anodes were tested and have shown good stability in reducing and oxidizing atmospheres at high temperatures [105, 106]. Combinations of chromium and titanium at the B-site have also been studied [97] but large polarization resistances were observed.

Apart from perovskite oxides, double perovskites, Rutiles and Spinel structured oxides have also been studied but there have not been too many formulations that match the performance of the Ni-YSZ cermets [73]. Oxide anodes are highly advantageous, as an all-ceramic SOFC will eliminate several of the thermal and chemical mismatch issues [73]. However, oxide materials are unable to conduct electrons rapidly enough when the materials are in the form of porous electrodes and when steam is present [2, 97]. The rate of catalytic activity on the oxides is not limited by the diffusion rate of O$_2^-$ ions as much as the rate of chemisorption of the fuel molecule onto the catalyst surface. Thus a lot of efforts are being focused on identifying catalytic additives to the surface [85].

2.2.3 Fuels and reaction mechanisms at the anode

The greatest strength of SOFCs over other fuel cells lies in the fact that theoretically any combustible material can be used as a fuel. Without the restriction of using only hydrogen as a fuel, which is the case in several other fuel cell technologies, significant cost savings can be achieved. Currently, 96% of the total hydrogen produced comes from reforming of hydrocarbons, and even with the most efficient conversions, 20% of the total fuel value is lost [2]. The potential
of working directly on hydrocarbon fuels is indeed tremendous in terms of cost and logistical benefits [2, 5, 89, 107-110]. There have also been studies looking into SOFCs operating on bio-gas and other fuel sources [111-113]. The most commonly studied fuel for SOFCs is CH$_4$ as natural gas, that is predominantly methane, is the most popular fuel choice for stationary power generation systems. Liquid hydrocarbons are also a viable option, and the ability to utilize liquid feed opens up other avenues of utility for SOFCs including electric vehicles. The production of electricity from the hydrocarbon source in an SOFC can be achieved in two ways. The hydrocarbon can either be completely oxidized, or it could be reformed first to syngas (CO, H$_2$) which is then oxidized [5, 87, 114]. The complete electrochemical oxidation of methane can be represented by the following reaction:

$$CH_4 + 3O^{2-} \leftrightarrow CO_2 + 2H_2O + 8e^- \quad \text{Reaction 8}$$

However this reaction does not occur through a single electrochemical step as can be seen from the large number of electrons generated. Thus it is more apt to refer to this process as direct utilization where in the absence of water or oxygen in the feed, all the methane is converted using the oxide ions coming in from the cathode side [85, 107, 115, 116]. Like all catalytic processes, these steps would lead to formation of intermediates on the surface. If the oxygen flux from the cathode is not high enough, coking could occur by the deposition of carbon on the anode surface. Coking could occur through several reactions including
disproportionation of the CO intermediate to form CO$_2$ and C, or the decomposition of methane [117].

Alternatively, internal-reforming of the fuel could also be a possibility where a mixture of steam and water are fed to the anode, and methane steam reforming first occurs to generate CO and H$_2$ which then are electrochemically oxidized at the Triple phase boundary[85]. However, steam addition has several deterrent effects on the anode including accelerated coarsening of the Ni particles. Internal reforming also reduces overall efficiency. The reforming reaction is also endothermic, thus creating temperature gradients in the electrode and leads to loss in performance as well as material degradation[2]. To overcome these detrimental effects, the research in this area is strongly driven to develop materials that can utilize hydrocarbons in dry conditions with resistance to coking or poisoning due to the other fuel contaminants including sulfur.
CHAPTER 3. Experimental Methods

3.1 Sample preparation

3.1.1 Perovskite oxides

The oxide materials were synthesized by standard solid state methods, that are well documented in literature [118]. The $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ oxides were synthesized by mixing the metal carbonate and oxide precursors, $\text{Co}_3\text{O}_4$ (Aldrich), $\text{La}_2\text{O}_3$ (Fisher), $\text{Fe}_2\text{O}_3$ (J.T. Baker), and $\text{SrCO}_3$ (Alfa Aesar). The metal oxide precursors were heat treated in air at 550°C with a 3 h isothermal hold time prior to use in order to remove any adsorbed species and to maintain the proper oxidation state. For each formulation, stoichiometric amounts of the precursors (10g total) were added to a ceramic jar, along with grinding media and distilled water. The grinding media used were .6- to 2.5-mm diameter zirconia grinding beads. The mixture was ball milled for 24hrs following which it was dried and crushed to powder. The powder was then heated to 1000°C for 48 hrs, wherein the High Temperature Solid State reaction takes place, to form the perovskite structure. For the catalysts described in CHAPTER 5 the additional B-site
dopants (Zn, Ni and Cu) were also included using their oxide precursors, in correct ratios, according to the desired composition.

3.1.2 NiO-YSZ

The NiO-YSZ samples were also synthesized using conventional solid-state methods. NiO (nanopowder, 99% purity) as well as Yttria Stabilized Zirconia (92% zirconia and 8% yttria) were both obtained from Sigma-Aldrich. The two were mixed in a ceramic jar to obtain a mixture containing 60% NiO and 40% of the mixed oxide on a mass basis. Zirconia grinding beads and distilled water were added to the jar and the mixture was ball-milled using a long roll jar mill (U.S. Stoneware) for 24 h at 120 revolutions per minute. The mixture was then dried and then crushed with a mortar and pestle and was calcined at 700°C for 5 hours.

For the additional metal oxide doping, the corresponding oxide precursors (CuO, V$_2$O$_4$ and SnO$_2$) were used and mixed along with the NiO and YSZ. The various precursors were weighed and added to the mixture in order to obtain a mixture containing 10% additional metal oxide, 50% NiO and 40% YSZ. The mixture was ball-milled along with the Zirconia beads and distilled water for 48 hours, and the then sieved, dried and crushed. Calcination was conducted at 700°C for 5 hrs.
3.2 Catalyst characterization

3.2.1 BET-surface area analysis

For the oxide catalysts, because of the low expected areas, Surface area measurements were made by the physical adsorption of Kr at 77 K on a Micromeritics ASAP 2010. The surface area was determined by fitting the desorption data with the Brunauer, Emmett, Teller (BET) isotherm. Nitrogen physisorption was used for the other catalysts. The catalyst surface area is a very important functionality because the degree and rate of adsorption of the various reactant species is strongly dependant on it. In general, reaction activity is proportional to the surface area. BET surface analysis of the pre-reaction and post-reaction catalysts can give us some insight on poisoning effects such as coking and sintering.

3.2.2 X-ray diffraction

The X-ray powder diffraction patterns were collected using a Bruker D8 Advance diffractometer. The radiation source used was a Cu K_{\alpha1} radiation source. The instrument is outfitted with an incident beam Ge (111) monochromator, incident beam Soller slits, and a Braun position sensitive detector (PSD). The current and the voltage were 50 mA and 40 kV. A 9-sample holder using polyethylene holders with a 0.5mm deep reservoir was used. The scan range was from 2-θ values of 20 to 90° at a step size of 0.0144° and a dwell time of 1 s. Other experimental parameters were as follows: 1° divergence slit,
0.5° anti-scatter slit, and 0.75” detector width. The unit cell parameters were determined using a least-squares fit.

For *in situ* measurements, a HTK 1200 sample holder with graphite windows was used. Samples were supported on an alumina holder with a 0.5 mm deep reservoir. A heating rate of 10°C/min and a 20 min hold time (5 min for solid-state reaction) before scanning at each temperature were also employed and the flow rate of air was 10 mL/min.

3.2.3 TGA-DSC

Thermogravimetric analyses were conducted using a Setaram TG-DSC111 instrument, which is capable of simultaneous microgravimetry as well as calorimetry. Flow balancing was performed in air at 350°C before each set of experiments. The sample (~85 mg) was loaded into Pt sample cups and the mass was allowed to equilibrate at room temperature to attain a steady mass before flow was started. The sample was heated to 750°C at 5°C/min in 15 mL/min flow of air and an isothermal hold was conducted for 30 min before being cooled at the same rate. The temperature program was repeated to eliminate the effects of any surface impurities during the first program. The mass change from the second program was then used to calculate the oxygen vacancy formation in the material.

3.2.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectra (XPS) for the La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ and La$_{0.6}$Sr$_{0.4}$(Co$_{0.18}$Fe$_{0.72}$Zn$_{0.1}$)O$_{3-\delta}$ were collected using a Kratos Ultra Axis
Spectrometer using a MgK_{\alpha} (1253.6 eV) radiation. The Mg anode was selected as the X-ray source to minimize the interference caused by Co and Fe Auger lines. Samples were ground into carbon tape for analysis. A slot aperture was used and the spectrometer was used in spectrum analyzer and hybrid lens mode. A charge neutralizer set at a current of 2.1 A, a bias of 1.3 V and a charge of 2.2 V was used. A survey scan was first acquired between 1200 and 0 eV to identify the surface components. Concurrent sweeps were then performed for La 3d, Sr 3d, Co 2p, Fe 2p, O 1s, Zn 2p and C 1s regions. The C 1s peak at 284.5 eV was used for binding energy correction. The C 1s peak at 284.5 was used to correct for binding energy shift and the deconvolution of the spectra was done with Gaussian curves using the XPS Peak 4.1 software. Elemental surface compositions were then calculated using transmission values and relative atomic sensitivity factors specific for the instrument and the Mg source.

For the anode studies, a Mono Al K_{\alpha} radiation (13 kV and 10 mA) under high vacuum (< 2X10^{-9} torr) was used due to the unavailability of the Mg K_{\alpha} source.

3.2.5 Mössbauer spectroscopy

Samples were examined at room temperature by Mössbauer spectroscopy using a conventional constant acceleration spectrometer with 2 GBq ^{57}Co/Rh source. The pulses corresponding to the 14.4 keV photons were accumulated in a 256-channel analyzer and were then sorted according to the velocity of the source varied either in the range of -5 to +5 mm.s^{-1} or in the range of -10 to +10
Isomer shifts, given with respect to $\alpha$Fe, and quadrupolar splittings were determined within the precision of 0.02 mm.s$^{-1}$. The accuracy for hyperfine field calculations was 0.2 T. The peaks positions of the spectra were determined by computer fits using a least-squares minimization assuming Lorentzian line shapes. The areas of the observed signals have been used to evaluate the relative populations of the different iron species, assuming an equal free recoil fraction for all species.

3.2.6 Methanol chemisorption and TPD

The methanol chemisorption and temperature programmed desorption (TPD) experiments were performed using a Thermo-Finnigan Trace Ultra differential scanning quadrupole (DSQ) gas chromatograph/mass spectrometer (GC/MS). Sample (~ 150 mg) was loaded in a quartz reactor, and was pretreated with a flow of 30 cmm of 20%O$_2$/He at 850°C for 20 min. The sample was then cooled to 50°C under the same flow. The methanol adsorption was conducted at 50°C to avoid effects of physical adsorption. A He stream was saturated with methanol using a homemade bubbler that was held at room temperature and the effluent from the bubbler was fed to a 15$\mu$L loop on a 6-port valve that was at 110°C for the pulses. All lines were heated to 100°C to prevent condensation.

Once the methanol pulses reached a steady area, the reactor was purged for an hr in He and then a temperature program was imposed on the reactor from 50-900°C at 10°C/min and the desorption products were monitored. Peak integration was performed using Grams AI software. The quantification of the
chemisorbed amounts were determined by integrating the 15 (CH₃), 29 (COH), and 31 (CH₃O) m/z fragments which are the major fragments for methanol. Antoine equation and ideal gas law were used to convert the pulse volume to amount of methanol. The adsorbed amount was converted to site density using the specific surface area assuming 1 site per adsorbed methanol molecule.

3.2.7 DRIFTS

DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) experiments were performed using a Thermoelectron Nicolet 6700 FTIR spectrometer equipped with a MCT detector and an environmental chamber. Spectra were obtained between 650 and 4000cm⁻¹ with a resolution of 4 cm⁻¹ and averaging 500 scans. Backgrounds were collected in He and then the methanol adsorption was conducted at 50°C for 1hr with a saturated He stream using a bubbler at room temperature. The TPD was then conducted in He, with spectra collected at every 50°C. The sample was held at each temperature for 5 minutes before collection of the spectra.

The in-situ reaction experiment was performed with a feed of 6% CH₃OH and 6% O₂ in He and the spectra were obtained from 50°C to 500°C in 50°C intervals. At each temperature another set of spectra were obtained after turning off the reactants flow and flushing the reactor with 30 ccm of He.
3.2.8 CO₂ temperature-programmed oxidation

CO₂ TPO experiments were performed after first reducing the catalyst with 20ccm of 10%H₂/He at 850°C for 30min and cooling it back down to room temperature. The ramp rate was 10°C/min. The TPO experiment was run with 30ccm of 10% CO₂/He and the sample was heated to 850°C at 10°C/min followed by an isothermal hold at 850°C for 30min. The effluent gas stream was analyzed using a Cirrus RGA-MS (MKS instruments) used in selected ion mode with a Faraday cup detector.

3.2.9 Temperature-programmed desorption (TPD) experiments

TPD experiments were conducted on a Thermo-Finnigan Trace Ultra differential scanning quadrupole (DSQ) gas chromatograph/mass spectrometer (GC/MS). For the Ni-YSZ samples (100mg) were loaded in quartz reactors and were pre-reduced in 30 mL/min of 10% H₂/He at 700°C. For the YSZ TPD experiments, 40mg of YSZ was used in order to work on an equal YSZ basis. The samples were held under reducing flow at 700°C for an 1hr, after which the flow was switched to 50ppm H₂S/N₂ and the H₂S adsorption was conducted for 5 hrs. The sample was then cooled to room temperature in He. In the case of the water co-adsorption, another adsorption step was conducted at room temperature under a flow of 10%H₂O/He obtained by bubbling He through a bubbler that was heated to 45°C. All lines were kept heated to prevent condensation. The flow was then switched to He at 30 mL/min and the system was purged for 1 h. The TPD was then conducted in He with heating to 800°C at 10°C/min and an isothermal hold for 10 min. Data for the GC/MS was obtained.
using selected ion mode (12, 16, 18, 28, 32, 33, 34, 44, 48, 60, 64, 76 and 80 monitored) and a 3 eV detector gain.

For the TPD experiments over the LSCF 6428 anode, the sample was first pretreated with 50 ppm H₂S at 700°C for an hour and then cooled to room temperature in N₂. The TPD was conducted next in He, heating the sample to 900°C. Data for the GC/MS was obtained using selected ion mode (12, 16, 18, 28, 32, 33, 34, 44, 48, 60, 64, 76 and 80 monitored) and a 3 eV detector gain.

3.2.10 XAFS studies

X-ray absorption fine structure (XAFS) spectroscopy was performed at the DuPont-Northwestern-Dow (DND) Collaborative Access Team (CAT) beamline 5-BM-D at the Advanced Photon Source at Argonne National Laboratory. The XAFS spectra were obtained at the Ni K edge for Ni-YSZ catalysts after a reduction treatment in 5%H₂/N₂ at 700°C for 1 hour, and after a subsequent treatment of 500ppm H₂S/N₂ for 5 hours. The analysis and fitting of the XAFS data were performed using WinXAS software [13].

For the oxide samples, the XAFS spectra were obtained at the Fe and Co K-edge.

3.2.11 TEM

Transmission electron microscopy was performed with a Philips Tecnai TF20. Samples were supported using a lacey-formvar carbon on a 200 mesh copper grid. The samples were dispersed in ethanol before being deposited on the support.
3.3 Reaction studies

3.3.1 Transient reaction studies

The temperature programmed reaction experiments were performed with an Autochem II 2920 (Micromeritics) automated catalyst characterization system. Samples were loaded into U-tube reactors and supported on a plug of quartz wool. The reaction effluent was analyzed by a Cirrus RGA-MS (MKS instruments). This instrument was used in selected ion mode with the electron multiplier detector. The reaction involved a temperature ramp at 10°C/min from 50 to 700°C where it was held isothermally for 4 h. The reactant flows for the methane oxidation were 50.0 mL (STP) / min of 5.0% CH₄ / 5.0% O₂ / He. For experiments with no gas phase oxygen, the feed consisted of 25.0 mL (STP) / min of 5.0% CH₄/He. For the methane steam reforming reaction the feed consisted of 52.5 mL (STP) / min of 4.8% CH₄ / 4.8% H₂O / He. The temperature was ramped to 700°C at 10°C/min. The catalyst was held at 700°C for 4 hours and the temperature was then ramped down to room temperature again under reaction conditions.

3.3.2 Steady-state reaction studies

The catalytic tests on the oxide materials were performed on an equal surface area (0.92 m²) basis using a quartz fixed-bed flow reactor. The catalysts were pretreated in 10%O₂/N₂ (50 cm³ STP/min) 850 °C for 20 min and cooled under the same flow. The feed percentages were CH₄/O₂/N₂/He = 5/5/40/50 (feed flow rate 50 cm³ STP/min). Nitrogen was used as the internal standard to
quantify volumetric flow rate change due to the stoichiometry of the reactions. 
For stoichiometric oxygen experiments, the CH₄/O₂ ratio was changed to 5/10.

For steam reforming reactions over Ni-YSZ catalysts, the steady-state catalytic tests were performed on 250mg of the catalyst in a quartz fixed-bed flow reactor. The catalysts were pretreated in 10%H₂/N₂ (50 cm³ STP/min) at 700 °C for an hour and then cooled under He. For the methane steam reforming tests, the feed percentages were CH₄/H₂O/N₂/He = 5/10/35/50 (feed flow rate 55 cm³ STP/min). The steam-to-carbon ratio was 1:2. N₂ was saturated by bubbling through water held at 54°C to obtain a flow of 10% H₂O in the feed. All lines were heated both before and after the reactor to prevent condensation.

The reactor effluent was analyzed using a Shimadzu 2014 Gas Chromatograph with a Flame Ionization Detector (FID), Pulse Discharge Helium Ionization Detector (PDHID) and Flame Photometric Detector (FPD). Separations were performed using He as the carrier gas using two columns: Supelco Q Plot (30m x 0.53mm, fused silica capillary column) and Carboxen™ 1010 Plot (30m x 0.53mm, fused silica capillary column). Reaction data were acquired after waiting at each temperature for steady state to be reached. Conversions and yields are defined as follows:

For oxidation:

\[
\% \text{ CH}_4 \text{ conversion} = \left( \frac{\text{moles of CH}_4 \text{ converted}}{\text{moles of CH}_4 \text{ in feed}} \right) \times 100
\]

\[
\% \text{ O}_2 \text{ conversion} = \left( \frac{\text{moles of O}_2 \text{ converted}}{\text{moles of O}_2 \text{ in feed}} \right) \times 100
\]
\[
\% CO_2 \text{ yield} = \left( \frac{\text{moles of } CO_2 \text{ formed}}{\text{moles of CH}_4 \text{ in feed}} \right) \times 100
\]

For steam reforming:

\[
\% CH_4 \text{ conversion} = \left( \frac{\text{moles of } CH_4 \text{ converted}}{\text{moles of CH}_4 \text{ in feed}} \right) \times 100
\]

\[
\% H_2 \text{ yield} = \left( \frac{\text{moles of } H_2 \text{ formed}}{4 \times \text{moles of } CH_4 \text{ in feed}} \right) \times 100
\]

\[
\% CO_2 \text{ yield} = \left( \frac{\text{moles of } CO_2 \text{ formed}}{\text{moles of CH}_4 \text{ in feed}} \right) \times 100
\]

\[
\% CO \text{ yield} = \left( \frac{\text{moles of CO formed}}{\text{moles of CH}_4 \text{ in feed}} \right) \times 100
\]
CHAPTER 4. Effect of Sr doping on LaFeO$_3$ based perovskite oxide materials

4.1 Motivation for studying Sr doped LaFeO$_3$ perovskites

Perovskite-type (ABO$_3$) oxide catalysts have been extensively studied over the past several years due to their oxygen storage and conduction properties [3, 119-121]. Their applications include several catalytic reactions such as total and partial oxidation reactions of hydrocarbons and volatile organics, photo-catalysis, and environmental applications such as SO$_2$ removal. They are also widely studied for their use in oxygen sensors and oxygen separation membranes where their anionic conductivity is utilized to achieve high purity separations [10, 11].

In recent years, there have been several studies on Co- and Fe-based perovskites as potential cathode catalysts. Defect structure and presence of oxygen vacancies can be attributed to the improved oxygen reduction and conduction capabilities in these materials [10]. The activity of these materials is co-limited by bulk ionic transport and the surface exchange kinetics of the oxygen reduction reaction (ORR) [8]. Thus, in these materials both the bulk oxygen pathway as well as the interfacial oxygen reduction kinetics play an important role. It has been shown that surface processes that are chemical in nature such as the surface oxygen exchange and oxygen surface diffusion, influence the performance of mixed conducting perovskite-type materials [8, 10, 122-125].
Recently, there has also been increased interest in studying these oxide materials as potential anode catalysts for SOFCs, examining them for their activity for methane oxidation reaction as well as electrochemical performances [6, 7, 91, 97, 105, 126]. Replacement of metal-based anodes with redox-stable metal oxides is promising for various reasons, among which is their resistance to coking under most conditions [90]. Moreover the increased ionic conductivity of these materials increases the extent of the triple phase boundary (TPB), which is the electrochemically active region where the oxide ions, the gas phase fuel reactants and the anode reactive sites come into contact. Also, in the case of oxides, the electrode material can be a single component as opposed to cermets, which helps overcome issues such as thermal conductivity mismatches and solid state reactions between the components [2]. However the electrical conductivities of these materials is pretty low which causes poor power densities and cell performances[2]. Studies have proven that the best approach would be to add a functional layer, thus utilizing two different materials for electrical conductivity and the anodic activity [73]. Most of the studies have focused on studying samples with 40% Sr dopant as potential anode materials[104]. However based on the properties and activity, this might not be the best candidate. Previous work in our research group has focused on studying the effect of Sr doping on the oxygen vacancy generation and oxygen content of the sample [127]. A linear trend was observed with increase in oxygen vacancy generation with increasing Sr content. A structural transition from rhombohedral to cubic symmetry was also observed with increasing Sr content. This work
focuses on extending the study of the effect of Sr dopant concentration on the properties of doped LaFeO$_3$ catalysts, as well as the effect of the oxygen mobility and oxygen activation properties on the methane oxidation activity.

4.2 Results

4.2.1 Bulk Structure under ambient conditions

The Mössbauer spectra of the doped La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_3$ samples are plotted in Fig. 4 and 5 and the calculated Mössbauer parameters are presented in Table 1. The results obtained are in good agreement with those already published in the literature [128-130]. At 20% Sr content the spectrum is characterized by antiferromagnetic sextuplet with broad lines and a doublet Figure 3(a). The hyperfine signal (relative intensity 76%) is characterized by an isomer shift of 0.35 mm.s$^{-1}$, typical of octahedrally coordinated Fe$^{3+}$ in high spin configuration. It can better be fitted considering a magnetic fields distribution (Figure 3b). The existence of such distribution should be related to the presence of the Fe$^{4+}$ cations and to a size distribution of the magnetic domains in relation with a random distribution of the later cations. The doublet (relative intensity 24%) is characterized by a small isomer shift ($\Delta_1$=mm.s$^{-1}$) and a zero quadrupolar splitting and has been attributed to Fe$^{4+}$ species [131].

At 40, 60 and 80 % of Sr dopant concentration, the Mössbauer spectra contain two doublets (Figure 4). One corresponding to the Fe$^{4+}$ species, already identified in the spectrum of the 20 % Sr containing sample, and one corresponding to Fe$^{3+}$ species. A transition from antiferromagnetic to paramagnetic behavior has occurred. The transition is accompanied with a
strong decrease of the isomer shift from 0.35 to 0.18 mm.s$^{-1}$ as also reported. In general, the relative intensity of the Fe$^{4+}$ doublet increased with the Sr content, but is not directly correlated to the Sr content, which can be explained by the formation of oxygen vacancies to balance the decrease in positive charge.

<table>
<thead>
<tr>
<th>Solid</th>
<th>$\delta$ (mm.s$^{-1}$)</th>
<th>$\Delta$ (mm.s$^{-1}$)</th>
<th>H (T)</th>
<th>Relative intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.35</td>
<td>0.00</td>
<td>47.3$^a$</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>0.00</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>40</td>
<td>0.18</td>
<td>0.34</td>
<td></td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>0.00</td>
<td></td>
<td>39</td>
</tr>
<tr>
<td>60</td>
<td>0.18</td>
<td>0.28</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>0.00</td>
<td></td>
<td>46</td>
</tr>
<tr>
<td>80</td>
<td>0.14</td>
<td>0.54</td>
<td></td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>0.00</td>
<td></td>
<td>57</td>
</tr>
</tbody>
</table>

$^a$: mean value of the magnetic fields distribution.
Figure 3 (a) $^{57}$Fe Mössbauer absorption spectra of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ , solid lines are derived from least-square fits; (b) hyperfine field histogram accounting for the magnetic sextet.
Figure 4 $^{57}$Fe Mössbauer absorption spectra of the La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ samples (a) $x = 0.4$ (b) $x = 0.6$ and (c) $x = 0.8$; solid lines are derived from least-square fits.
4.2.2 Surface composition

Surface compositions as a function of dopant concentration were studied using XPS. The spectra for the A- and B-site cations as well as oxygen are shown in Figure 5. The peaks were deconvoluted to calculate surface compositions and the details are reported in Table 2. In the La 3d region, two different oxidation states for La were identified. A trivalent oxide with the 3d_{5/2} peak at 833.3 eV as well as a higher binding energy feature at 837 eV which has been linked to surface hydroxyl groups [65, 132]. While there is no significant shift in the peaks, the area decreases as expected with increasing Sr dopant concentration.

In the Sr 3d region, we see two peaks associated with SrO (133 eV) as well a sub-oxide species (131.5 eV) at lower binding energies[65]. The concentration of these two species on the surface increases steadily with increasing Sr content. The oxygen 1s region showed interesting shifts with increasing Sr content. While the higher binding energy peak corresponds to chemisorbed oxygen, the lower binding energy peak is attributed to oxide ions in the lattice. Looking at the overall composition of the surface as indicated by the percentage values in Table 2, it appears that the surface is enriched in oxygen as compared to the bulk. With increase in the Sr doping level, it is seen that the lower binding energy oxygen peak decreases in size and follows a similar trend to the TPD data in our previous work[127], wherein at higher Sr dopant levels, the sample is sub-
stoichiometric in oxygen at room temperature. The Fe 2p region shows a band wide enough to include contributions from Fe in 4+ (712 eV) and 3+ (710 eV) oxidation states.

Figure 5 X-ray photoelectron spectra for La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$
Table 2 X-ray photoelectron spectroscopy results summary

<table>
<thead>
<tr>
<th>Region</th>
<th>Position (eV)</th>
<th>Surface Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x = 0.2</td>
<td>x = 0.4</td>
</tr>
<tr>
<td>La 3d</td>
<td>833.3 833.8</td>
<td>833.7 833.6</td>
</tr>
<tr>
<td></td>
<td>836.9 837.6</td>
<td>837.3 837.3</td>
</tr>
<tr>
<td>Total</td>
<td>9.7 5.4</td>
<td>5.5 3.5</td>
</tr>
<tr>
<td>Sr 3d</td>
<td>131.9 132.1</td>
<td>131.7 131.4</td>
</tr>
<tr>
<td></td>
<td>133.4 133.6</td>
<td>132.6 133.0</td>
</tr>
<tr>
<td>Total</td>
<td>4.0 9.7</td>
<td>9.2 10.0</td>
</tr>
<tr>
<td>Co 2p</td>
<td>780.2 781.0</td>
<td>780.8 780.0</td>
</tr>
<tr>
<td>Fe 2p</td>
<td>710.2 710.7</td>
<td>710.4 710.1</td>
</tr>
<tr>
<td>O 1s</td>
<td>528.6 528.3</td>
<td>528.3 529.0</td>
</tr>
<tr>
<td></td>
<td>531.5 531.7</td>
<td>531.3 531.3</td>
</tr>
<tr>
<td>Total</td>
<td>77.4 77.3</td>
<td>74.9 77.3</td>
</tr>
</tbody>
</table>

4.2.3 CO$_2$ temperature programmed oxidation (TPO)

CO$_2$ TPO has been used before to study oxygen mobility over perovskite oxides [40]. The mechanism of CO$_2$ dissociation and CO evolution involves formation of surface oxygen species, which then need to be interfacially transported into the lattice. Thus activity for the CO$_2$ reduction/dissociation will be a good indicator of the rate at which surface oxygen moves into the lattice. It is commonly known that the oxygen reduction reaction at the SOFC cathode is co-limited by both surface reaction as well as the interfacial transport [8]. Figure 6 shows the $m/z = 28$ (CO evolution) signals from the CO$_2$ TPO experiments obtained over pre-reduced catalysts. It is seen that there are two distinct features
in the TPO, a sharp low temperature peak at around 600° C and a broad shoulder at higher temperature at around 800°C. These features can be attributed to different oxygen sites and vacancies in the catalyst surface and bulk. Both features increase in intensity with increasing Sr content. The oxygen TPD results [127] also showed two peaks attributed to different redox couples in the catalyst. The mechanism of the CO₂ TPO is said to involve oxygen vacancies in the lattice and the two features we see in the CO₂ evolution are possibly associated with different lattice sites. The high temperature feature involves the sites that are harder to re-oxidize and these sites become more accessible for the TPO with increasing oxygen content due to increased oxygen mobility. Although there are differences in the CO₂ evolution intensity as well as temperature as a function of the Sr doping level, the sample with the highest Sr doping shows the most pronounced increase in CO₂ dissociation.
4.2.4 Reaction activity

Methane oxidation activity of the catalysts was studied as a function of Sr dopant level over the La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ catalysts using both transient and steady state experiments. The results from the transient Temperature Programmed Reaction (TPRxn) experiments are shown in Figure 7. The signals are normalized in order to view the features better. CO$_2$ and H$_2$O were the primary products of oxidation over all catalysts. Also, partial oxidation products such as CO were not observed in any case. The methane conversion takes off...
over all catalysts at around 400°C. The oxygen conversion and CO₂ light-off temperatures are also around 400°C. At lower temperatures before reaction takes off, we see a peak in the oxygen signal, indicating desorption of oxygen from the catalyst. The extent of desorption increases with increasing Sr content. At the lower dopant concentrations, there is almost no desorption. When methane conversion takes off close to 400°C, we see drops in the 32 signal with a corresponding rise in the CO₂ signal. Oxygen is the limiting reactant in these reactions as the feed contains sub-stoichiometric oxygen. In all cases, there is a local maximum in the CO₂ signal and a local minimum in the methane signal, and this is due to the oxygen desorption from the lattice. The size of the maxima and minima is a function of the Sr dopant concentration. At higher temperatures, the gas phase oxygen and the surface oxygen vacancies eventually equilibrate to reach a steady activity, and CO₂ and methane signals reach constant values determined by the oxygen concentration in the feed. At this point, the oxygen signal is zero.

In order to study this effect further, another methane oxidation experiment where no gas phase oxygen was supplied to the system was conducted. In this case, the partial oxidation products, H₂ and CO are the primary products of reaction. The 28 signal from the experiment is shown in Figure 8. A window of activity is observed for the methane oxidation to CO and H₂. In all cases, onset of activity takes place at around 650°C and there are multiple peaks corresponding to different oxygen sites in the lattice. The temperature window of activity extends to much higher temperatures with increasing Sr dopant concentrations. For the
sample with 80% Sr, it is seen that the largest feature is observed at 800°C. Also, the lower temperature features are comparable in area to the sample with lower Sr content. Comparing the overall CO evolution from the sample it is observed that it is a linear function of the Sr content. With increasing Sr content, we see that more oxygen in the sample lattice becomes available for the oxidation reaction. This implies that there is increased oxygen mobility in the samples with higher oxygen content, which facilitates higher methane oxidation activity.

Steady-state activity was also studied for methane oxidation. As seen in the transient experiments, for these feed conditions, CO₂ and H₂O were the favored products of oxidation, although small amounts of CO and H₂ were also observed (less than 1% yield). The CO₂ yields and oxygen conversions are presented in Figure 9 a & b respectively. Complete oxygen conversion was reached over all catalysts by 550°C. The feed was sub-stoichiometric in oxygen, and hence the maximum methane conversion and CO₂ yield was limited by the availability of oxygen. At lower temperatures, we see that the samples with the higher Sr dopant levels show a higher oxygen conversion than the La-rich catalysts. This can be attributed to increased oxygen mobility in these samples, due to increased oxygen vacancy formation and hence higher oxygen activation. Apparent oxygen activation energies calculated from an Arrhenius plot shown in Figure 9 c are tabulated in Table 3. We see a significant decrease in activation energies with increasing Sr content. The oxygen vacancies as well as increased oxygen mobility in these materials improve surface oxygen activation.
Table 3 Oxygen activation energies from steady-state methane oxidation on La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$

<table>
<thead>
<tr>
<th>X</th>
<th>Ea kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>128</td>
</tr>
<tr>
<td>0.4</td>
<td>121</td>
</tr>
<tr>
<td>0.6</td>
<td>70</td>
</tr>
<tr>
<td>0.8</td>
<td>57</td>
</tr>
</tbody>
</table>
Figure 7  TPRxn- methane oxidation over La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_3$.  a) Methane  b) O$_2$ and c) CO$_2$ signals.
Figure 7 (continued)

c) CO₂ Signal
44 m/z

Normalized mass signal (a.u.)

Temperature (°C)
Figure 8  TPRxn: methane oxidation with lattice oxygen : CO signal for \( \text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \). a) \( x = 0.2 \) b) \( x = 0.4 \) c) \( x = 0.6 \) d) \( x = 0.8 \)
(continued)

Figure 9  Steady-state methane oxidation a) Methane conversion b) Oxygen Conversion c) Arrhenius Calculations
Figure 9 (continued)

b) \[ \ln(\text{rate of } O_2 \text{ conversion (mol g}^{-1} \text{ s}^{-1})] \]

\[ O_2 \text{ conversion (%)} \]

\[ \text{Temperature (°C)} \]

\[ X = 0.8 \]
\[ X = 0.6 \]
\[ X = 0.2 \]
\[ X = 0.4 \]

c) \[ \ln(\text{rate of } O_2 \text{ conversion (mol g}^{-1} \text{ s}^{-1})] \]

\[ \frac{1}{T} \text{ (K}^{-1}) \]
4.3 Discussion

4.3.1 Oxygen mobility and oxidation activity

The samples showed good activity for the methane oxidation reaction and only complete oxidation products were observed. Most of the studies that included methane oxidation over these materials have been conducted under conditions of excess oxygen [133-135]. In our studies, oxygen served as the limiting reactant, and reaction tests were performed under these conditions to simulate conditions in an SOFC anode, where the supply of oxygen is limited by the rate at which it is conducted through the electrolyte to the anode. Operating at these conditions provided good insight into the differences in oxygen and methane activation as a function of temperature and Sr content in these samples. It is established in the literature that the oxidation of methane over perovskite oxides takes place through an interfacial process where the lattice oxygen is the source of the active oxygen involved in the reaction. A Mars-Van Krevelen redox cycle is involved, wherein the bulk oxygen migrates to the surface and is involved in the oxidation of the surface adsorbate, while it is replaced in bulk by the gas phase oxygen[121, 135]. Thus the mobility of the oxide ions within the bulk plays a vital role in the catalysis mechanism. This difference in mobility is more apparent under limiting oxygen conditions. We observe increased oxygen activation and methane oxidation activity at lower temperatures with the higher Sr content and oxygen mobility. At higher temperatures we see the activity go
through a maxima as the bulk oxygen content of the sample equilibrates. This is further explained by the results observed, as shown in Figure 13, when the oxidation is carried out with no external oxygen feed. These results are further put into context by other studies where the methane oxidation selectivity was found to be a strong function of lattice oxygen content [136]. Thus, experiments in limited oxygen can be useful in studying the catalytic activity of these materials as potential SOFC anodes. It is known that increasing Sr content in these materials increases the thermal expansion coefficient (TEC) of these materials significantly over that of Yttria-Stabilized Zirconia, which is the state of the art electrolyte material in Solid Oxide Fuel cells. However, the TEC can be controlled with method of synthesis as well as pretreatment parameters [3]. It is important to optimize the composition for maximum activity as well as compatibility.
CHAPTER 5. Effect of additional B-site transition metal doping on oxygen transport and activation characteristics

5.1 Motivation

Mixed-conducting perovskite oxides of the general form ABO$_3$ have been studied for their unique surface and bulk properties that make them useful for several applications. They have been studied as oxygen sensors and oxygen separation membranes where their anionic conductivity is utilized to achieve high purity separations [10, 11]. They have also been studied for their catalytic activity for total and partial oxidation reactions [3, 119-121]. Their electronic conductivity as well as the ability to conduct oxide ions makes them a very popular choice as cathode materials for Solid Oxide Fuel Cells (SOFCs)[3, 25]. The present work focuses on developing new formulations for improved cathode performance for SOFCs.

The cathode reaction in an SOFC is the activation and reduction of oxygen. The cathode catalyst, apart from having very good activity for oxygen reduction, should also be stable in an oxidizing environment. It must also have high electronic conductivity. The choice of material is also limited by the Thermal Expansion coefficient (TEC) and compatibility with the electrolyte, which is usually yttrium-stabilized zirconia (YSZ). The current limitations to SOFCs include cost, durability and slow cathode kinetics [3]. There is also an increased
effort to lower the operating temperature of SOFCs to develop intermediate
temperature SOFCs (IT-SOFC) in order to solve the materials cost and durability
issues. This implies the need for more active cathode materials that can activate
and reduce oxygen at lower temperatures. The state of the art strontium-doped
lanthanum manganite (LSM) SOFC cathodes lack oxygen mobility and hence
limit the cathode performance. Significant effort has been focused on replacing
LSM with mixed conducting perovskite oxides [54, 137-142]. While Lanthanum
Ferrite- and Cobaltite-based formulations are the most commonly studied
materials, there are many studies on other oxide structures as well [25].

The performance of the SOFC cathode is co-limited by surface kinetics as
well as bulk oxygen ion mobility[8, 123]. In oxide materials, oxygen ions are
transported by the random hopping of oxygen vacancies in the lattice. Oxygen
vacancies can be induced by doping of the materials. This is done by replacing
the normally trivalent A-site (La) with a divalent cation (Sr) as well as substituting
the B-site with more reducible cations such as Fe and Co. Oxygen vacancy
formation in Co, Fe, and Mn perovskite-type materials has been studied and the
ease of forming oxygen vacancies has been found to increase in the following
order: Mn < Fe < Co [40, 143, 144]. Solid solutions of Co and Fe have also been
studied to take advantage of the stability of Fe and conductivity of Co [145-148].

Our previous work has focused on Sr- and Co-doped LaFeO₃ materials. The
bulk-structure and surface properties of the materials were studied as a function
of dopant concentrations [41, 65, 66, 127]. It was found that the oxygen vacancy
generation and oxygen-activation and surface kinetics in La₀.₆Sr₀.₄CoₓFe₁₋ₓO₃₋δ is
a non-linear function of Co dopant concentration and was due to an electronic structure transition induced at higher Co loadings [41, 66]. While oxygen vacancy generation was enhanced with increasing Sr dopant concentration, the TEC incompatibility with YSZ was an issue at higher temperatures[127]. The current work examines the effect of additional doping of the B-site with aliovalent cations such as Zn, Ni and Cu on the oxygen activation properties. By substituting with lower valent cations, and making the B-site more reducible, the oxygen vacancy generation capabilities could be enhanced. While the use of Cu- and Ni-containing perovskites as cathode catalysts [44-50], as well as the effect of Cr and Ti dopants on La$_{1-x}$Sr$_x$Co$_y$Fe$_{1-y}$O$_{3-\delta}$ (LSCF) [149] have been studied before, there has not been much work in examining additional B-site dopants in LSCF catalysts. This work investigates the oxygen vacancy generation and oxygen activation properties with the addition of the B-site dopants.

5.2 Results and Discussion

5.2.1 Bulk structure

The catalysts of the general formula La$_{0.6}$Sr$_{0.4}$(Co$_{0.18}$Fe$_{0.72}$X$_{0.1}$)O$_{3-\delta}$ were synthesized where X was Zn, Ni or Cu. These catalysts were synthesized using La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF 6428) as the baseline material, where 10% of the B-site was replaced with aliovalent atoms such as Zn, Ni and Cu (LSCF-Zn, LSCF-Ni, LSCF-Cu). The X-ray diffraction patterns of the catalysts, which were obtained at room temperature, are shown in Figure 10. A single perovskite
structure is identified in all three catalysts, and it can be seen that the catalysts show the characteristic peaks associated with a rhombohedral structure. The diffraction pattern of the baseline LSCF 6428 catalyst is also included for reference and on comparison we can see that there are no impurity phases observed in the catalyst bulk. The variations in peak intensities show slight variations in crystallinity between the samples. But overall, the synthesis procedure was successful in introducing the dopant atom into the catalyst bulk.
Figure 10 X-ray diffraction patterns of the catalysts with LSCF 6428 included for comparison.

The formation of oxygen vacancies, in these perovskite materials, is critical to their ability to activate and transport oxygen [41, 144, 150]. Thus, oxygen vacancy generation is an important screening test to determine the activity of a catalyst for oxygen reduction and oxidation reactions. Thermogravimetric analysis was used to study the evolution of oxygen vacancies in the synthesized catalysts as a function of temperature in air. From our previous studies over these materials we have seen that dopant concentration and both A-site doping
with Sr as well as B-site doping with Co have a strong influence on oxygen vacancy generation [41, 127]. The results from the TGA experiments are shown in Figure 11. LSCF 6428 is the baseline catalyst, and the oxygen content (3-δ) of the sample is plotted as a function of temperature. It is seen that with the substitution of Co and Fe on the B-site of the ABO$_3$ perovskite oxides, with a different/lower valence atom, the formation of oxygen vacancies in the materials is enhanced. The new catalysts showed higher vacancy content as well as the evolution of vacancies at lower temperatures as compared to the LSCF 6428. The LSCF-Zn sample showed the best results, with oxygen vacancy creation at lower temperatures (400°C) as well as a much higher vacancy content at 700°C compared to LSCF-6428. Oxygen vacancies are created by incorporating charge imbalances in materials. In perovskite materials there are several approaches to vacancy creation. Vacancy generation increases with temperature as well as reducing atmospheres. Substitution of the trivalent La with divalent Sr ions and the choice of the B-site atoms influences the vacancy generation behavior. Substituting Fe in the B-site with more easily reducible Co atoms has shown an increase in vacancy generation. However, an optimum Co content exists, influenced by electronic structure transitions around the Fe atom [66]. With further doping of the B-site with lower-valence and more reducible atoms, the oxygen vacancy generation is enhanced as seen in the data presented. There also seems to be a relationship between the size of the size of the dopant cation (Zn>Cu>Ni) and vacancy generation. Since the LSCF-Zn sample showed most promise, further investigation of this catalyst was undertaken.
In general Fe-based perovskites are known to have rhombohedral or cubic structures depending on the composition of the A and B-sites [145, 146]. We have previously observed a rhombohedral-to-cubic phase transition with increase in temperature over the Co-doped Lanthanum Ferrite based materials[41]. This transition is an important factor determining the oxygen activation and mobility in these materials as, in general, cubic structures are more symmetric leading to a more random distribution of the vacancies and hence a higher oxygen ion

**Figure 11** Oxygen vacancy generation in air as a function of temperature measured by TGA. LSCF 6428 catalyst served as the baseline for comparison.
mobility. For LSCF 6428, this transition temperature was found to be around 550°C[41]. The phase transition for LSCF-Zn was studied using in-situ X-ray diffraction study in air. The results are presented in Figure 12. The diffraction patterns for the three main cubic Miller indices, (111), (211), (220), are shown. At lower temperatures, a rhombohedral phase is observed, identified based on the broadness of the peak indicating the presence of multiple peaks indicating the presence of multiple diffraction lines. With increasing temperature, the peaks become sharper, and a transition to a cubic phase is observed denoted by a sharp, single peak. And this transition occurs at comparatively lower temperatures close to 400-500°C for the LSCF-Zn sample. Moreover, the transition was also reversible and the sample reverts back to a rhombohedral phase upon cooling. The shift of the peaks to lower 2-θ values with increasing temperature indicates thermal expansion and assuming a linear expansion of the lattice, the TEC value was calculated. The TEC was calculated to be 12.3ppm/°C. This value is comparable to that calculate for LSCF 6428 (11.6ppm/°C) as well as the value for YSZ (10ppm/°C) which is the standard electrolyte for SOFCs [41]. This TEC match with the electrolyte is an important criterion for choosing electrode materials in SOFCs.
Figure 12 X-ray diffraction patterns of LSCF-Zn as a function of temperature in air – the Miller indices corresponding to the cubic lattice are shown.

EXAFS analysis was also conducted on the samples at the Fe-edge to understand the local coordination effects as well as oxidation state of the Fe as a function of the B-site doping. The normalized EXAFS spectra are shown in Figure 13. The spectra look fairly well matched for the 5 samples studied. The XANES region is shown in detail in Figure 14. It is seen that the intensity of the whiteline at 7.13 keV decreases with the additional B-site doping. This decrease is accompanied by a slight shift of the absorption edge to higher energy values. The trend within the dopants is consistent with the TGA results where the Zn
doped sample showed the biggest change. The shift in the K-edge corresponds to an increase in the valence state of the iron. With increase in valence state, the electrons are bound more strongly to the nucleus, thus requiring higher energies. The inset in Figure 14 shows the zoom in of the absorption edge to show the shift in edge better. While the shift in edges is not very high, it is in the range of what is expected for a Fe +3 to +4 transition [25]. An increase in the % of Fe atoms in the +4 state implies a greater charge imbalance at the B-site and hence implies that there will be higher oxygen vacancy generation. These results support the TGA studies and validate our hypothesis of increased vacancy formation with additional B-site doping.
Figure 13 Normalized Fe K-edge X-ray absorption spectra
5.2.2 Surface properties

Surface processes such as oxygen exchange and surface diffusion play a key role in the activity as well as the performance of mixed conducting oxides[10, 122]. For SOFC cathodes, it is known that the performance is co-limited by ionic diffusion as well as the activation of gas-phase oxygen on the cathode surface[123]. The surface properties of LSCF-Zn were characterized and the results are presented in this section. X-ray Photoelectron Spectroscopy was conducted over the catalyst to determine the surface composition of the various
components in the catalyst. The XPS spectra of the various regions are shown in Figure 15. The surface concentrations of Co and Zn in the sample were below the detection limits of the instrument. The peak positions and the elemental surface compositions were determined based on the deconvolution of the spectra and the data are presented in Table 4. As seen before in these materials, there is a surface Sr enrichment [65]. In the Sr 3d region, Sr was found to exist in two divalent forms with the 3d_{5/2} binding energies at 131.9 and 133.4 eV and can be attributed to Sr in a perovskite and a sub-oxide phase[65]. Similarly two La oxide phases were identified in the La 3d region with a trivalent oxide (833.3eV) as well as a lower oxidation species (836.9eV) commonly attributed to hydroxyl formation on the surface[132]. The Fe 2p region shows a band wide enough to include contributions from Fe in 4+ (712 eV) and 3+ (710 eV) oxidation states. The oxygen region showed two distinct peaks at 528.6 eV and 531.5 eV. The lower binding-energy peak is associated with the lattice oxide ions whereas the higher binding energy peak corresponds to chemisorbed oxygen[65]. The ratio of the two oxygen regions as well as the positions of the peaks in the other regions correspond well with the values observed with 20% Co doping on the B-site in our previous work. The additional transition metal dopant has minor effects on peak position shifting the oxygen peaks to lower binding energies as well as a slightly lower oxygen surface content which implies a more reducible surface. Overall, it is seen that the surface compositions of the elements are significantly different from the bulk, and the surface is enriched with Sr and Oxygen. These results are similar to that observed over doped perovskite oxides before[65].
Table 4 XPS peak parameters from peak fitting and deconvolution of the surface species in LSCF-Zn.
Methanol has been used successfully in our previous work in characterizing the surface of the perovskite oxide as well quantifying and identifying the nature of the surface sites. Pulsed methanol chemisorption experiments were conducted over the LSCF-Zn sample and the chemisorption pulses are shown in Figure 16. The pulses corresponding to the important methanol fragments are shown. The 28 m/z signal is used to show the valve switch noise associated with each pulse. From the three fragments, it was estimated that an average of 1.25 pulses was adsorbed over the sample. The adsorption amount was converted into surface site-density using the mass specific surface area value and was found to be
0.726 sites /nm$^2$. While the site density is low as compared to traditional metal oxides, it was close to the 1.03 sites/nm$^2$ that was observed for the baseline LSCF 6428 sample[65].

Temperature-programmed desorption experiments were performed subsequently over the LSCF-Zn catalyst following the chemisorption, once the peak areas of the pulses were constant indicating a saturated surface. The results of the TPD with the key-species are shown in Figure 17. CO$_2$ (m/z =44)
desorbs from the catalyst as a result of oxidation of chemisorbed methanol on basic sites on the catalyst surface[17]. Two peaks were observed, one at lower temperatures close to 300°C which is similar to what was previously observed over the LSCF 6428 catalyst. The higher temperature CO₂ indicates surface heterogeneity, and the presence of another set of basic sites which have a stronger interaction with the adsorbed methanol with a stabilization of the surface species. The 29 m/z signal also showed interesting features. Apart from a peak at lower temperature, corresponding to the intact Lewis-bound methanol adducts that are molecularly adsorbed methanol that corresponds well with the previously observed values[18], there is also peak at 460°C. The peaks are much lower in intensity than the CO₂ peaks observed. The high temperature feature was not observed in any of the other Methanol fragments (m/z = 15, 32, 31, 28) indicating the presence of a different desorbing species. Studies establishing the use of methanol as a probe molecule have shown that the nature of products from oxidation of methanol reflects on the type of surface sites. Redox sites are known to oxidatively dehydrogenate methanol to produce formaldehyde [151]. This feature could be attributed to formaldehyde formation on a redox site on the LSCF-Zn catalyst, as m/z=29 is the major formaldehyde fragment also. Formaldehyde wasn’t observed in our previous work studying the LSCF 6428 catalysts[65]. Methanol TPD experiment was conducted and observed using DRIFTS to understand this further. The DRIFTS spectra are shown in Figure 18 a and b. The DRIFTS TPD confirms the presence of both basic sites as well as Lewis sites. The presence of molecularly adsorbed methanol is confirmed by
vibrations corresponding to CH$_3$ (~2900 cm$^{-1}$) as well as a strong CO vibration (~1050 cm$^{-1}$). Moreover CO$_2$ (~2350 cm$^{-1}$) was also observed starting at 100°C.

Comparing these spectra with those observed over the LSCF 6428 in our previous work [65], it is seen that the CO$_2$ evolution starts at lower temperatures over the LSCF-Zn catalyst. Moreover, the CH$_3$ vibrations as well as the CO$_2$ persist until higher temperatures also, again reinforcing the existence of a heterogeneous surface. The CH$_3$ vibrations are shown in more detail in Figure 19. Vibrations corresponding to CH$_3$ stretch (3007, 2951, 2922 cm$^{-1}$) and bending modes (2866, 2842, 2870 cm$^{-1}$) were observed. Lewis-bound methanol species are identified by the sharp bands at 2951 cm$^{-1}$ and 2845 cm$^{-1}$ while the other CH$_3$ vibrations are associated with surface methoxy species [65]. These vibrations diminish over temperature, but do not completely leave the surface until 400°C. No vibrations were observed to indicate the presence of aldehyde species on the surface. It must be noted though that due to sample being very dark and due to the low signal intensities, assignment of the weak bands at higher temperatures becomes difficult. In general, DRIFTS TPD results reiterates our earlier conclusions about the stabilization of the methoxy species on the catalyst surface and the heterogeneity of the surface.

In another experiment, methanol oxidation was studied in-situ in DRIFTS where methanol and oxygen were fed to the catalyst in the IR chamber and the DRIFTS data was obtained as a function of temperature. At each temperature, additional spectra were collected after stopping the reactor feed and flushing with He for 8 mins. This was done to be able to distinguish between the contributions
from the gas-phase species and the surface species. The results of this experiment are shown in Figure 20. In the presence of methanol and oxygen, we observe features corresponding to surface hydroxyl groups (3710 cm\(^{-1}\)) as well as carbonyl groups (1030 cm\(^{-1}\)) signifying the presence of dissociatively adsorbed methanol groups. Vibrations corresponding to gas phase water are also observed (in 3800-3600 cm\(^{-1}\) and 1800-1300 cm\(^{-1}\) region). CH\(_3\) vibrations are also observed in the 2800 cm\(^{-1}\) - 2900 cm\(^{-1}\) region. The sharp peaks corresponding to the Lewis-bound methanol species were also observed. Starting from 100°C the doublet indicating the presence of gas phase CO\(_2\) is also observed (2300 cm\(^{-1}\)). Additionally we also see a vibration at around 1770 cm\(^{-1}\) at 100°C that is a characteristic of aldehyde species [152]. This species is short-lived on the surface however and is not observed after the He flush (Figure 20 c). The presence of the peak however affirms the assignment of the high temperature peak in the 29 m/z signal in the TPD to the formation of formaldehyde on the LSCF-Zn surface. The oxidative dehydrogenation in the redox sites is known to follow a Mars–van Krevelen mechanism and it has been established that oxides exhibiting high oxygen mobility can be selective to redox products[151]. The presence of a more reduced surface with the addition of the dopant Zn atom could be the cause for a greater number of redox sites as opposed to LSCF 6428 where formaldehyde formation were not detected [65].
Figure 17 Temperature programmed desorption following chemisorption of methanol over LSCF-Zn.
Figure 18 DRIFTS during Methanol TPD over LSCF-Zn a) low wavenumber region b) high wavenumber region.
Figure 18 (continued)
Figure 19 CH$_3$ vibrations at 50°C for the adsorbed methanol species observed in DRIFTS.
Figure 20  In-situ methanol oxidation reaction in DRIFTS over LSCF-Zn catalyst
a) Spectra in the low wave number region b) in the high wave number region c) After a 5 min flush in He.
Figure 20 (continued)

b)
Figure 20 (continued)

c)
5.2.3 Oxygen activation and oxidation activity

CO₂ TPO has been used earlier to study the oxygen mobility of perovskite oxides [40]. The mechanism of CO₂ dissociation and CO evolution involves formation of oxygen species in the surface which are then interfacially incorporated into the lattice. Activity for the CO₂ dissociation and reduction to CO, is thus a good indicator of the rate at which surface oxygen moves into the lattice. Figure 21 shows the m/z = 28 (CO) signals from the CO₂ TPO experiments obtained over the LSCF-Zn catalyst. The results for LSCF 6428 are also presented for comparison. It is seen that there are two distinct features in the TPO, a sharp low temperature peak at around 600°C and a broad shoulder at higher temperatures. These features can be attributed to different oxygen sites and vacancies in the catalyst surface and bulk. There is a decrease in peak temperatures in the LSCF-Zn catalyst as compared to LSCF 6428. The mechanism of the CO₂ TPO involves oxygen vacancies in the lattice and the two features we see in the CO₂ evolution are possibly associated with different lattice sites. The high temperature feature involves the sites that are harder to re-oxidize and these sites become more accessible for the TPO with increasing oxygen content due to increased oxygen mobility. For the LSCF-Zn catalyst, we see that the high temperature feature shows slightly higher intensities and both the peaks have moved to lower temperatures indicating greater accessibility of
the lattice oxygen with the additional B-site doping and subsequently higher oxygen mobility.

**Figure 21** Comparison of the CO$_2$ TPO activity of the catalysts.

Steady-state methane oxidation experiments with sub-stoichiometric oxygen in the feed have been used successfully before in studying differences in
oxygen activation in perovskite oxides [153]. The oxidation activity of LSCF-Zn was studied and is compared with La_{0.6}Sr_{0.4}MnO_3 (LSM) and LSCF 6428. In all three cases CO_2 and H_2O were the primary products with negligible traces of CO and H_2 produced (<1%). The methane and oxygen conversion activities are compared in Figure 22 a & b respectively. From oxygen TPD studies [153] and TGA results presented here, we know that the oxygen vacancy generation varies as LSM < LSCF 6428 < LSCF-Zn. The same trend was observed in the methane oxidation activity also, where the LSCF-Zn catalyst showed much higher methane and oxygen conversions. The CO_2 yield followed the same trend. In order to study the oxygen activation in more details, oxygen turnover frequencies were calculated for the LSCF-Zn and LSCF 6428 samples based on the site densities obtained from the methanol chemisorption experiments, and the TOF as a function of temperature are plotted in Figure 23a. Apparent activation energies were calculated based on the Arrhenius plots shown in Figure 23b, and the calculated activation energy values are tabulated in Table 5. The activation energy for oxygen is significantly lower in the LSCF-Zn catalysts and much higher oxygen turnovers are observed. Many of the studies in the literature studying Methane oxidation have been conducted under conditions of excess oxygen [133-135]. Using oxygen as a limiting reactant helped us gain good insight into the oxygen activation differences between the samples. It is well known that methane oxidation takes place through an interfacial process where the lattice oxygen is the source of the active oxygen involved in the reaction, in perovskite oxides. It involves a Mars-Van Krevelen redox cycle where the surface
adsorbate is oxidized by the bulk oxygen from the lattice, migrating to the surface, which is subsequently replenished by the gas phase oxygen[121, 135]. Thus the mobility of the oxide ions within the bulk is the key in the catalysis mechanism. Thus higher oxygen activation in the LSCF-Zn sample can be attributed to increased oxygen mobility.

Figure 22 Comparison of the methane oxidation activity of the catalysts. a) CH₄ conversion rate b) O₂ conversion rate.
Figure 22 (continued)

b)
Figure 23  a) Oxygen turnover rate and b) Oxygen Activation comparison between LSCF-Zn and LSCF 6428.
Figure 23 (continued)

b)

\[ y = -8.9695x + 6.48 \quad R^2 = 0.9759 \]

\[ y = -15.511x + 15.035 \quad R^2 = 0.9663 \]
<table>
<thead>
<tr>
<th>Oxygen activation</th>
<th>Ea (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCF -Zn</td>
<td>75</td>
</tr>
<tr>
<td>LSCF-6428</td>
<td>128</td>
</tr>
</tbody>
</table>

**Table 5** Apparent oxygen activation energies
5.2.4 Conclusions

Additional B-site doping of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ increase the oxygen activation and vacancy generation properties. The Zn-doped catalyst showed best performance. TEC values calculated from in-situ XRD show good thermal compatibility with YSZ. Surface characterization using methanol as a probe molecule showed the presence of surface heterogeneity with the presence of both basic and Lewis sites. CO$_2$ TPO experiments showed improved oxygen activation and mobility in the samples, and the methane oxidation activity showed the increased oxygen activation and catalytic activity of the LSCF-Zn sample when compared to the baseline catalyst. These results suggest that this catalyst is a potential cathode catalyst for IT- SOFCs with good oxygen activation properties at lower temperatures as compared to the state of the art LSM and LSCF cathodes.
CHAPTER 6. Effect of H$_2$O on Sulfur poisoning and catalytic activity of Ni-YSZ catalysts

6.1 Motivation

Solid Oxide Fuel Cells are gaining popularity for direct use with hydrocarbon fuels and as on-board reformers in other energy systems. A Ni/YSZ cermet electrode is the state of the art anode in SOFCs because of its low cost, chemical stability at reducing atmospheres and at high temperatures as well as good thermal expansion match with YSZ[67]. The cermet structure ensures porosity and thermal compatibility with the electrolyte. Ni serves as an excellent catalyst for the electrochemical oxidation of hydrogen. The YSZ provides both ionic conductivity as well as support[2]. Since the oxide ions are the species transported through the electrolyte, a SOFC has the potential of operating on any combustible fuel[2]. The elevated operating temperature of SOFCs along with the ability to utilize CO as a fuel enables the operation of these fuel cells directly on hydrocarbon fuels. The hydrocarbons are first catalytically converted to CO and H$_2$ and then electrochemical oxidation takes place[3]. The ability to reform hydrocarbons significantly reduces losses due to external reforming systems as well as simplifies overall system design and construction. The major problem with directly operating on hydrocarbons is the propensity towards carbon formation via cracking over the catalyst surface. Ni catalyses carbon formation in kinetically controlled regimes even though thermodynamics predicts otherwise[70].
Moreover sulfur tolerance is an issue with Ni/YSZ. The Ni cermets are poisoned by H₂S concentrations even in the ppm range[78].

S poisoning of Ni catalysts has been the focus of many studies[154, 155]. However despite several studies, the kinetic mechanism of poisoning in SOFC anodes remains unclear[80]. It is important to be able to understand the deactivation mechanisms due to S and C in order to develop mitigation techniques as well as to develop S and coke tolerant and stable alloy formulations. While studies showed that even 5 ppm H₂S was enough to cause a significant drop in the overall cell voltage and hence SOFC performance[84], it was also found that this poisoning effect was strongly dependant on the operating temperature. At lower temperatures, the poisoning effect of H₂S becomes more and more irreversible[84]. At high concentrations (> 100 ppm), performance losses are attributed to the formation of bulk Ni-S species [156-159]. Although the H₂S degradation mechanism at low concentrations (< 100 ppm) is not as well understood, experimental and theoretical studies suggest the formation of adsorbed S on Ni (which are unstable when H₂S is removed from the feed) as the source of deactivation [158, 160-163].

More recently, there have been several experimental and theoretical studies focusing on modeling the sulfur poisoning and regeneration in the SOFC anode[76, 81, 82, 136]. Most of these studies have focused on studying electrochemical deactivation and sulfur adsorption and coverage over the anode. It is also important to study the catalytic effects on the Ni-YSZ, especially when operating on hydrocarbon fuels, as there exists a network of reactions taking
place at the anode. In our previous work on the effect of H\textsubscript{2}S on Ni-YSZ catalysts, where a complete study of the network of reactions was conducted, it was found that reactions involving water were more susceptible to deactivation due to sulfur poisoning. Also, in a recent study it was found that the sites for catalytic methane reforming and electrochemical oxidation on Ni-YSZ were different and also had different tolerances to sulfur poisoning. Thus it is important to consider both these sites while doing deactivation studies. In a lot of cases fuel cells working on hydrocarbon feed first go through a pre-reformer, or work as internally reforming cells, thus making these studies important. Also to prevent coking, these systems are fed excess steam, thus making the effect of H\textsubscript{2}O on S deactivation an important factor to consider [87, 164]. The current work focuses on investigating the sites affected by H\textsubscript{2}S poisoning as well as the effect of H\textsubscript{2}O on the deactivation.

6.2 Results

6.2.1 Temperature programmed reaction study

The effect of sulfur poisoning on the catalytic activity of Ni-YSZ was first studied using temperature programmed reaction studies. The activity of the Ni-YSZ sample for methane steam reforming reaction after a pretreatment with 50ppm H\textsubscript{2}S at 700°C for 5 hours was studied first and the outlet of the reactor was analyzed using a Mass Spectrometer. Profiles for CH\textsubscript{4}, CO, H\textsubscript{2} and CO\textsubscript{2} are shown in Figure 24. It can be seen that during the temperature ramp, we observe an initial activity for the steam reforming reaction, starting at around 350°C, seen by the drop in the CH\textsubscript{4} signal, accompanied by a corresponding rise in the H\textsubscript{2},
CO and CO$_2$ signals. However by 500°C the activity goes through a maxima and by 700°C, there is a complete loss of activity. Also, no activity was observed when the temperature is ramped back down. This maxima in reaction activity has been previously observed in our studies over these catalysts which also indicated an adverse effect of the H$_2$S pretreatment especially in reactions involving water as a reactant [79]. The results of these experiments indicate that there are irreversible changes taking place on the surface of the sulfur treated catalysts in the presence of water at higher temperatures leading to loss in activity. Also from the ramp down, it is seen that this effect is not reversible.

Figure 24  Methane Steam Reforming TPRxn over Ni-YSZ after pre-treatment with 50 ppm H$_2$S at 700°C.
6.2.2 Steady-state reaction studies

Steady–state steam reforming experiments were conducted over the Ni-YSZ after a pretreatment with 50ppm H$_2$S at 700°C for 5 hours and the results are summarized in Figure 25. The activity of the catalyst is poor and very low conversions and yields are observed. However beyond 700°C we see the activity slowly picking up indicating that sulfur is evolving from the catalyst, freeing the catalytic sites for reaction. The detection limit of the GC however restricted the detection and quantification of the sulfur species desorbing.

![Figure 25](image)

**Figure 25** Steady-state methane steam reforming over Ni-YSZ after pretreatment with 50 ppm H$_2$S at 700°C
In contrast, when the steady-state runs were performed over the sulfur-free catalyst, methane conversions very close to equilibrium are observed at the higher temperatures, as shown in Figure 26a. From the product yields shown in Figure 26b, it is seen that r-WGS reaction takes off over the catalysts at higher temperatures, and CO and H₂ are the primary products. Carbon balances indicate that there is significant coking over the catalyst, (the coking characteristics are discussed in section 6.2.5). When 50 ppm of H₂S is introduced into the feed stream, we see a drastic drop in activity with both methane conversion and H₂ yield reducing severely with just 2 hours of exposure to H₂S as seen in Figure 27.
Figure 26 Steady-state methane steam reforming over Ni-YSZ – a) Methane conversion b) product yields
Methane oxidation experiments were also conducted over this catalyst and the results from steady-state methane oxidation runs are shown in Figure 28. These reaction tests were run feeding sub-stoichiometric oxygen to mimic the conditions in the SOFC anode. Close to 100% O₂ conversions were obtained over the sample by around 450°C. Close to 50% CO₂ yields were also observed by this temperature, consistent with the reaction stoichiometry, as seen in Figure 28 b. The CH₄ conversion, however, was also close to 100% and significant amounts of CO and H₂ were also formed indicating the existence a network of reactions including partial methane oxidation as well as methane decomposition.
With the introduction of 50 ppm H₂S into the feed stream, it is seen that the methane conversion and CO and H₂ yields drop significantly within a few hours of sulfur exposure. However, oxygen conversion and CO₂ remain nearly the same indicating that the sites for oxidation to CO₂ are less susceptible to attack by H₂S on Ni-YSZ.

(a)

Figure 28  Steady-state methane oxidation with sub-stoichiometric oxygen, over Ni-YSZ – effect of H₂S on a) conversion and b) yield.

(continued)
To understand this effect further, another oxidation study was performed using a CH$_4$:O$_2$ ratio of 1:2, which is the stoichiometric value for complete oxidation to CO$_2$. The results of this experiment are summarized in Figure 6. It is seen that close to complete oxygen and methane conversions were observed by 500°C, accompanied by CO$_2$ yields of over 90%. CO$_2$ and H$_2$O were the only major products, with negligible amounts of CO and H$_2$ also detected. The activity for oxidation did not drop and remained stable when 50 ppm H$_2$S was added to the feed stream even after 6 hrs of exposure. This result validates our hypothesis that oxidation sites on the Ni-YSZ catalyst are less susceptible to attack by sulfur.
Figure 29  Steady-state methane oxidation with stoichiometric oxygen over Ni-YSZ – effect of H₂S on Methane conversion, Oxygen conversion and CO₂ yield.

6.2.3 Effect of H₂O on sulfur poisoning

These initial results as well as our previous work [79] studying the effect of H₂S on activity of Ni-YSZ indicate that the deactivation is more severe in reactions involving water. To understand this phenomenon better, Temperature
Programmed Desorption (TPD) experiments were performed over the catalyst, and the results are summarized in Figure 30. The adsorbed sulfur in the sample evolved in the form of sulfur oxides in the TPD. From the m/z=64 signal (SO₂), it is seen that there is significantly more sulfur desorbing from the catalyst surface when H₂O is co-adsorbed. Moreover, it is also seen from the SO₃ signals (Figure 30 b) that, there is some sulfur species desorbing from the catalyst at lower temperatures when H₂O is co-adsorbed. These results indicate that there is greater surface interaction of H₂S in the presence of water and also a lower temperature surface rearrangement taking place over the Ni-YSZ catalyst. When these TPD experiments were repeated over YSZ, it was seen that there is significant sulfur adsorption-desorption on the oxide surface also. From the data in Figure 31 a, it is seen that there is increased desorption in the presence of water even on the oxide surface. There is not much SO₃ coming off the surface, and moreover it is seen that there is desorption at much lower temperatures in both cases. These results suggest that over the Ni-YSZ catalyst, there is bound to be a lot of desorption and re-adsorption of sulfur species from the YSZ surface onto the Ni sites, especially in the presence of water.
Figure 30 TPD results over Ni-YSZ showing a) SO₂ and b) SO₃ mass signals.
Figure 31 TPD results over YSZ showing a) SO$_2$ and b) SO$_3$ mass signals.
To verify this conclusion, the stoichiometric methane oxidation experiments were repeated with and without water (1%) in the feed stream. Under dry conditions, over 95% conversion is obtained as shown in Figure 32. The first two data points in the figure correspond to dry run at 700°C. Again, CO₂ and H₂O are the only products formed. Once water is introduced into the feed stream (starting at the third data point), it is seen that the conversion remains unchanged. However when 50ppm H₂S is introduced into the feed stream a drop in activity is observed (data points 4-7). However, comparing Figure 32 with Figure 27, it is seen that the drop in activity is not that severe. Oxidation sites are less affected by sulfur, and there is also lower H₂S adsorption on the Ni sites in the absence of water. After the initial drop with H₂S exposure, the activity seems to hold. When water is removed from the feed (data point 8 onwards), the activity improves, but initial conversion levels are reached only when H₂S is removed from the feed stream. These results again suggest a surface re-arrangement introduced by the presence of water in the feed stream.
6.2.4 XAFS studies

The XAFS studies at the Ni K-edge over the samples with and without sulfur exposure were conducted to understand the interactions between the Ni atoms and adsorbed sulfur. The EXAFS region doesn’t show many differences between the two samples as seen in Figure 33. The sample spectrum is very similar to that of the Ni-foil standard, which is included for comparison. Fitting for the Ni-Ni coordination using the Ni foil standard showed that the samples contained large Ni particles very close to bulk metallic Ni. The results from the fit are summarized in Table 6. The values obtained are close to those obtained for the Ni-Ni shell in
the literature [83, 165]. NiS and Ni\textsubscript{3}S\textsubscript{2} were also studied as references, however
the Ni edge EXAFS spectra of the samples resembled the Ni foil and the effect of sulfur seemed to be more of a local effect, due to which it wasn’t observable in the EXAFS spectra.

The XANES region showed more interesting results. It is seen that with exposure to sulfur, the Ni atoms get more oxidized. This result is in agreement with earlier XPS results from our group[79]. The % of Ni in the +2 oxidation state, calculated by fitting the XANES spectra with Ni foil and NiO standards, increases with exposure to sulfur further confirming that the poisoning due to sulfur in the Ni-YSZ anodes is a catalytic effect more than a case of physical surface coverage effect.
Figure 33  EXAFS analysis of Ni-YSZ with and without H₂S exposure
a) Normalized EXAFS spectra  b) k²-weighted Fourier Transform of EXAFS function in magnitude.
Figure 34 XANES analysis of Ni-YSZ with and without H$_2$S a) XANES spectra b) oxidation state of Ni in samples.
6.2.5 Coking studies

Ni-based catalysts are known for their proclivity to coking and are also used in carbon fiber growth. The catalysts were characterized for carbon deposition post reaction using TEM microscopy. The catalysts were studied after holding on the methane steam reforming conditions at 700°C for 5 hours. Large particles over 50nm in size were observed completely encased in a long fiber like structure. On composition analysis using EDX analysis, it was deduced that these were Ni particles encased in carbon fibers as shown in Figure 35.

The % of CH₄ going to carbon during the steam reforming reaction was calculated from the carbon balances and is summarized in Figure 36. It is seen that close to 25-30% of the methane in the feed goes to carbon on the catalyst surface. Interestingly, with the introduction of H₂S into the feed, this % goes
down to zero, again reiterating the conclusion that sulfur blocks Ni sites catalyzing decomposition and carbon formation routes.

Figure 35 Post reaction TEM images and EDX analysis showing coke formation on Ni-YSZ after MSR.
Figure 36 Effect of H$_2$S on coking over catalysts - % CH$_4$ going to C deposits from C balance in the Steady-state MSR studies.
6.3 Discussion

6.3.1 Effect of H$_2$S on reaction activity

The effect of H$_2$S on the catalytic activity of Ni-YSZ was studied in detail in our previous work. The activity for all the reactions involved in the anodic reaction network, and the effect of H$_2$S for each of these reactions was studied using temperature programmed reaction experiments[79]. It was seen that the effect of sulfur was more severe on reactions involving water as a reactant. Methane steam reforming and water-gas reaction were affected more than Methane oxidation and r-WGS reaction. From the various characterization tools used, it was seen that the S attacked certain Ni sites on the catalyst. The current work, confirms these results through steady state experiments with H$_2$S in the feed stream under reaction conditions, and shows that the oxidation sites on the Ni-YSZ are more immune to attack by H$_2$S. Under stoichiometric oxygen flow, as shown in Figure 29, it is seen that steady activity is maintained over the catalyst despite the presence of 50 ppm H$_2$S in the feed stream for up to 6 hours. The conversions and product yields are not affected by the H$_2$S. On the contrary, in the case of oxidation under sub-stoichiometric oxygen flow, which is closer to SOFC operating conditions wherein the oxygen is the limiting reactant with the oxide ions coming in from the cathode, we see an effect of the sulfur poisoning on the CO and H$_2$ yields. This implies that the sites for CO and H$_2$ formation through a decomposition pathway are blocked by S.

These findings fit well with some recent work in the literature studying the sulfur poisoning on Ni-YSZ under SOFC operating conditions. Rostrup-Nielsen et
al identified through experimental studies that sites for methane conversion and
electrochemical oxidation are different on the Ni-YSZ cermet anodes, and that
the electrochemical sites are not poisoned by sulfur\cite{166}. Our results point out
that even the catalytic oxidation sites on the Ni-YSZ are not susceptible to attack
by sulfur. Methane oxidation is unaffected by sulfur in the presence of
stoichiometric oxygen. When H$_2$O is introduced into the feed stream, it is seen
that there is increased susceptibility to H$_2$S poisoning. In Figure 32 it is seen that
the methane oxidation activity drops immediately, when H$_2$S is introduced into
the feed stream in the presence of H$_2$O. This indicates migration of the S to more
active sites or reconstruction of the surface sites at certain temperatures with
H$_2$O exposure. The H$_2$S TPD experiments confirm the hypothesis as we observe
an increased stabilization of adsorbed S on the catalyst surface with H$_2$O co-
adsorption, as well as some low temperature desorption-reconstruction effects.
Reconstruction of surface Ni by S has been studied previously, where it has been
proved that reactions are structure sensitive over Ni \cite{167, 168}.

6.3.2 Effect of H$_2$S on coking

Ni based catalysts are commonly used for carbon fiber growth and are
known to undergo coke formation in the presence of carbonaceous fuel. The
mechanism of coking on Ni, involves the deposition of C on the catalyst surface,
followed by dissolution into the carbon bulk, followed by precipitation of C fiber
from the catalyst surface\cite{2}. We observed long carbon fibers on the Ni-YSZ
catalysts after holding under steam reforming conditions for 5 hrs. The % of CH$_4$
going to C deposition was calculated from our GC balances. In the presence of
H₂S, we see that the % CH₄ being converted to C decreases significantly. S passivation is known to control C formation in Ni based catalysts [167, 169-172]. S preferentially binds to the surface step sites in Ni catalysts which are also the most active sites for coke formation and steam reforming activity [154, 155]. Thus, with the introduction of S into the reaction stream the CH₄ decomposition reaction pathway is blocked and we see a drop in the CO and H₂ yields during the methane oxidation reaction in sub-stoichiometric oxygen feeds.

Sulfur poisoning at a fuel cell anode under fuel cell operating conditions, will also depend on electrode potential, as well as the possibility of electrochemically oxidizing the sulfur at the electrolyte interface.
CHAPTER 7. Sulfur tolerant anode materials

7.1 Bi-metallic anode catalysts

Motivation

The Ni-YSZ catalysts, while demonstrating excellent activity for the anode reactions also have several inherent problems associated with them. Ni sinters at high temperatures and is also known to show propensity toward carbon fiber formation [70]. Moreover, poisoning due to sulfur is another major issue wherein the Ni cermets are poisoned by H$_2$S concentrations in the ppm range[78]. Finding ways to mitigate these problems can not only reduce the cost of the fuel cell, but reduce the balance-of-plant requirements for gas cleanup.

Several efforts are undergoing currently to develop improved formulations or replacements to the Ni-YSZ anodes. There have been attempts where the Ni has been replaced by other metals such as Cu and Cu-CeO$_2$-YSZ anodes have been tested[89]. While Cu does not catalyze carbon fiber formation and displays better sulfur tolerance, it doesn’t match the electrochemical activity of Ni and has a lower melting point and sintering issues[173]. Bi- and tri-metallic anodes alloying Ni with other metals including Cu, Fe and Co have been studied [94, 95] and these have shown initial promise. Sulfur containing materials such as CuFe$_2$S$_4$, NiFe$_2$S$_4$, WS$_2$, CuCo$_2$S$_4$, and CoS$_2$ were tested for sulfur tolerance and activity, but it was found that deactivation occurred when long term studies
were performed [96]. Research in our own group has shown that the effect of H$_2$S at low concentration remains at the catalyst surface and also poisoning by sulfur improves resistance to coking [79]. These results provide the motivation for studying surface modification of NiO-YSZ to improve sulfur tolerance. Additional anode modifiers that show promise including molybdenum, cobalt and tin, can actively adsorb and/or oxidize H$_2$S, thereby offsetting the fraction of nickel affected.

Results and Discussion

New bimetallic catalyst formulations were synthesized to study the coking and sulfur tolerance characteristics. These were formulated replacing some of the Ni with an additional transition metal to achieve synergistic tolerance to sulfur. The catalysts had a composition of 10% X-50%NiO 40%YSZ, where X was SnO, V$_2$O$_4$ and CuO. Sn is known in the literature to have synergistic effects with Ni in coking [2] and vanadium based oxide materials have also been shown to oxidize H$_2$S [3]. Previous work had also showed that Cu-based catalysts did not form coke in the presence of carbonaceous fuels [2]. The catalysts were synthesized by mixing the precursors in stoichiometric proportions and conducting a high temperature solid state reaction at 900°C.

Activity for methane steam reforming

Steady state methane steam reforming reaction studies were performed on an equal mass basis. The catalysts were all pre-reduced before activity testing. The feed consisted of 4.5% CH$_4$ and 9% H$_2$O, 41% N$_2$ and balance He. N$_2$ was used as the internal standard to quantify the volume change with conversion. The
methane conversion over the 3 catalysts is shown in Figure 37. The activity of the Ni-YS catalyst is also included as a reference for comparison. It can be seen that while the low temperature activity of the Cu- and Sn- containing catalyst is poor for this reaction, at higher temperatures and especially at 700 °C all catalysts have comparable methane conversion and reaction activity. The V-containing catalyst showed higher methane conversions than the baseline Ni-YSZ catalyst.

The activity on the introduction of H₂S into the feed stream is shown in Figure 38. When 50 ppm H₂S is introduced into the feed, it can be seen that the activity of the Ni-YSZ catalyst falls immediately. The methane conversions drop in all the new formulations also, but the degree of loss in activity varies significantly between the samples. While the V-containing catalyst shows promising behavior, it can be seen that the activity remains on a downward trend for the catalyst in the presence of sulfur. Moreover, the coking tolerance of the catalysts was studied by calculating the % of methane converted to carbon deposits based on the carbon balance. The results are shown in Figure 39. While the V-doped Ni-YSZ showed high methane conversions, it is seen that significant portions of the methane converted to coke, making the catalyst susceptible to deactivation and hence is undesirable as an SOFC anode material. It is found that the addition of Cu and Sn however significantly lower carbon formation as compared to the Ni-YSZ and hence are promising approaches to coke mitigation. However, as seen from the previous figure, these catalysts lack tolerance to sulfur poisoning.
Figure 37  Methane conversion during steady state steam reforming reaction
Figure 38 Methane conversion during steady state steam reforming reaction – Effect of H₂S
7.1.1.a Steady state methane oxidation activity testing

The steady state activity of the anode catalysts for the methane oxidation reaction was also tested. These tests were conducted with sub-stoichiometric oxygen in the feed similar to our previous experiments on Ni-YSZ as described in 6.2.2. The methane and oxygen conversions are shown in Figure 40 and Figure 41. It can be seen that the CuO-containing catalyst shows very good activity for the oxidation reaction at lower temperatures and is comparable to that of Ni-YSZ. The Sn- and V- containing catalysts show poor low temperature oxidation activity, however the activity catches up at higher temperatures. It is also seen that complete oxygen conversion is achieved in all catalysts at 650 °C. The CO and CO₂ yields are shown in Figure 42 and Figure 43. At lower temperatures,
CO₂ and water are the primary products of oxidation. At higher temperatures, CO yields are very significant. The H₂ yield (not shown) also increases. This CO could be a result of reverse-water gas shift reaction. CO and H₂ could also be produced by partial oxidation of the species formed from the decomposition of methane.

When H₂S is added to the feed stream, it is seen that there is a loss in methane conversion as shown in Figure 44. However, when we look at the product distribution, it is seen, in Figure 45 and Figure 46, that while the CO yield decreases significantly, the CO₂ yield remains almost a constant. These results are comparable to what was observed over Ni-YSZ in a similar experiment as discussed in 6.2.2. With the sub-stoichiometric oxygen in the feed, at higher temperatures, significant portion of the methane is converted to CO and H₂ via decomposition routes, and once again it is seen that sulfur blocks the sites on these catalysts catalyzing the reaction of methane to CO and H₂ and thus the CO yields falls to zero upon exposure to H₂S.
Figure 40 Steady-state methane oxidation activity: methane conversion
Figure 41 Steady-state methane oxidation activity: oxygen conversion
Figure 42 Steady-state methane oxidation activity: CO yield
Figure 43 Steady-state methane oxidation activity: CO$_2$ yield
Figure 44 Steady-state methane oxidation activity: methane conversion - effect of H$_2$S.
Figure 45 Steady-state methane oxidation activity: CO yield - effect of H$_2$S.
Figure 46 Steady-state methane oxidation activity: CO₂ yield- effect of H₂S.

Conclusions

The addition of a dopant metal to the NiO-YSZ did not cause significant changes in the activity for methane reforming and oxidation reactions. However, with the addition of Sn and Cu, there was a significant lowering of the carbon deposition. All the formulations however showed loss in activity with exposure to sulfur.
7.2 Perovskite anode materials

7.2.1 Motivation

There are significant findings in the literature that suggest the use of alternative, nickel-free and red-ox stable anodes for SOFCs [73]. Replacement of metal-based anodes with redox stable metal oxides is a very promising approach. Oxides do not form carbon under most conditions [90]. Moreover the increased ionic conductivity of these materials increases the extent of the triple phase boundary (TPB), which is the electrochemically active region where the oxide ions, the gas phase fuel reactants and the anode reactive sites come into contact. Also, in the case of oxides the electrode material can be a single component as opposed to cermets, which helps overcome issues such as thermal conductivity mismatches and solid state reactions between the components [2]. Ceria and doped ceria are excellent oxidation catalysts and their effectiveness as anode catalysts has been widely studied [86, 91]. However the electrical conductivities of these materials is pretty low which causes poor power densities and cell performance[2]. A functional layer of doped ceria placed between the anode and electrolyte improves performance by expanding the TPB [73]. Several materials including Flourites, perovskite-based anodes as well as pyrochlore materials have been explored as Ni-YSZ replacements[173]. Perovskites of the formula La\(_x\)Sr\(_{1-x}\)VO\(_{3+\delta}\) (LSV) have shown selectivity towards oxidation of H\(_2\)S even in the presence of H\(_2\) [103]. However these materials have poor catalytic activity for hydrocarbon oxidation/reforming. By and large, oxide materials are unable to conduct electrons rapidly enough when the materials are
in the form of porous electrodes and when steam is present[2, 97]. Of these materials SrTiO$_3$ shows good promise[100]. Doping the A site in these materials could help induce mixed conductivity thus enabling the expansion of the active catalytic area as well as improving electrochemical performance[174]. LSCF type perovskite materials have also been studied as potential anodes [7, 104]. The biggest problem associated with these oxide anodes is their stability in reducing conditions. LaCrO$_3$ based anodes were tested and have shown good stability in reducing and oxidizing atmospheres at high temperatures[105, 106]. There have been very few studies looking at sulfur tolerance of perovskite oxide materials. The presented work explores the effect of H$_2$S on methane oxidation activity of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF 6428) and also looks at the interaction of sulfur on the catalyst surface. LSCF 6428 was chosen based on the previous work on these catalysts as the optimum catalyst composition looking into both the dopant concentrations as well as the TEC values[41, 65, 175].

7.2.2 Results and Discussion

7.2.2.a Reaction activity and sulfur tolerance

The activity of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF 6428) was studied for the methane oxidation as well as reforming reactions. It was seen that the perovskite oxide materials do not have an activity for the steam reforming reaction. However, they are active in catalyzing the oxidation reactions. The results of methane oxidation with sub-stoichiometric oxygen (CH$_4$ : O$_2$ = 1:1) over LSCF 6428 is shown in Figure 47. CO$_2$ and H$_2$O were the only products formed. Even
in oxygen deficient environments, total oxidation is preferred. It is seen that complete oxygen conversion is reached by 500°C and the CH₄ conversion and CO₂ yield follow stoichiometry. Methane conversion was around 50%, and was the maximum achievable given the feed stoichiometry. The CO₂ yields followed stoichiometry, implying that all the methane converted was forming CO₂ and there were no side undesirable side-reactions taking place. This is contrary to what was observed over Ni-YSZ or the bi-metallic compositions. (6.2.2 and 7.1.1.a). With the introduction of 50ppm H₂S into the feed at 700°C, it is seen that the activity remains stable. Methane conversions and CO₂ yields hold in the presence of H₂S even up to 10 hrs on stream. This is a very promising result that establishes the stability of the catalyst and it’s tolerance to sulfur poisoning.

The % of CH₄ being converted to CO₂ during methane oxidation reaction for the oxide catalyst is shown in Figure 48 and is compared to the performance of the Ni-YSZ catalyst. While at lower temperatures, the NiO YSZ catalyst show higher yield, at temperatures close to SOFC operating temperature, the LSCF catalyst shows activity equal to that of the NiO YSZ.

While comparing the coking behavior of the two catalysts, in Figure 49, it is seen that there is significantly lower coke formation over the oxide catalysts, thus showing its potential as a stable catalyst in the presence of carbonaceous fuels. The % of CH₄ going to C was calculated using the carbon balances from the GC runs. Also, in the case of oxide catalysts, most of the Methane converted goes to CO₂, whereas in the case of NiO YSZ there is significant C formation as well as products of partial oxidation such as CO and H₂ are formed which leads
to loss of electrons. The testing of the catalysts under sub-stoichiometric oxygen conditions helps us understand the behavior of the catalysts in an actual SOFC better, as the $O^{2-}$ ions are the limiting reactants at the anode.

Figure 47  Methane oxidation over LSCF 6428 using sub-stoichiometric oxygen
Figure 48  Activity comparison of LSCF 6428 with Ni-YSZ for methane oxidation
The activity of the oxide catalyst was also tested with stoichiometric oxygen in the feed and the results are shown in Figure 50. It is seen that close to 100% CH$_4$ conversions and CO$_2$ yields are obtained. From the carbon balances, it was seen that the % of CH$_4$ going to C was close to zero at all temperatures. With the introduction of 50 ppm H$_2$S at 700°C, it was seen that the activity held and there was no loss in conversions/yield. These results show good promise for the replacement of the state of the art NiO YSZ catalysts with oxide based catalysts.

Figure 49 Comparison of carbon formation during methane oxidation between LSCF 6428 and NiO YSZ.
To verify the stability of the catalyst in the presence of water, the stoichiometric methane oxidation experiments were repeated with and without water (1%) in the feed stream. Under dry conditions, over 95% conversion is obtained as shown in Figure 51. Again, CO$_2$ and H$_2$O are the only products formed. Once water is introduced into the feed stream (starting at the second data point), it is seen that the conversion remains unchanged. When 50ppm H$_2$S is introduced into the feed stream there is a very slight decrease in activity but this drop is almost negligible when compared to that observed in Ni-YSZ catalyst in Figure 32 and Figure 27. This slight drop in activity (<5%) could be attribute to a site coverage and competitive adsorption effect on the catalyst in the presence of water.
of water. When the water is removed from the feed stream (point 5), the activity goes back to the initial value. This is different from what was observed over the Ni-YSZ catalyst wherein the activity did not go back to the initial conversion % until H₂S was removed from the feed stream (Figure 32). The activity of the catalyst for the methane oxidation reaction remains steady for 10 hrs in the presence of H₂S and this result is very promising as the effect of water on this catalyst seems less pronounced than Ni-YSZ.

**Figure 51** Effect of water on methane oxidation and sulfur poisoning on LSCF

6428
7.2.2.b Interaction of S with catalyst surface

X-ray Photoelectron Spectroscopy was used to study the interactions of sulfur with the catalyst surface. In the previous section it was seen that the activity for methane oxidation over the LSCF 6428 catalyst was maintained even in the presence of 50 ppm H₂S for up to 10 hrs. It is important to understand the nature of interactions of the catalyst with the sulfur as this would help us identify the active sites for the oxidation reaction better. The XPS spectra of the catalyst were obtained both with and without a pretreatment of 500ppm H₂S in N₂ at 700°C. Surface compositions as a function of dopant concentration were studied using XPS. The deconvoluted XPS spectra for the various regions are shown in Figures 52 and Figure 57. The % surface compositions of the deconvoluted species were calculated and are tabulated in Table 7. Noticeable differences were observed in the XPS spectra with the H₂S exposure. The most significant differences were observed in the La 4d and Sr 3d region. In the La 4d region, two different oxidation states for La were identified for the LSCF 6428 catalyst at 101.2 ev as well as a higher binding energy feature at 103.8 ev. Previously, the two oxidation states have been identified at the 3d region for LSCF 6428 as a trivalent La and a higher binding energy state that is linked to surface hydroxyl groups [65, 132]. With the sulfur exposure two peaks at 100 and 102.5 eV were observed. The peak at 100 eV can be assigned to La in the +3 oxidation state [132]. The higher binding energy peak could be attributed to a lower oxidation state La associated with surface sulfide or sulfate groups.
In the Sr 3d region, we see two peaks 3d$_{5/2}$ associated with SrO (133 eV) as well a sub-oxide species (131.7 eV) at lower binding energies[65]. With the sulfur exposure, the Sr region changed significantly. The spectra was deconvoluted to reveal three different peaks. The two previously observed oxide and sub-oxide peaks were present. In addition, there was a peak at 132.6 eV that could be attributed to a surface sulfide species[176]. The presence of SrCO$_3$ can also not be ruled out.

The oxygen 1s region (Figure 54) also showed interesting shifts with S exposure. While the higher binding energy peak corresponds to chemisorbed oxygen, the lower binding energy peak is attributed to oxide ions in the lattice. Oxygen associated with sulfate groups also has a peak at around 532 eV making the deconvolution of the higher binding peak tricky. However, it is easily seen that there is a significant increase in the higher binding energy peak with exposure to H$_2$S indicating the presence of surface sulfate groups. This result is further confirmed by looking at the S 2p region in Figure 57 where a peak at 167.7 eV associated with S in the form of surface sulfates is observed[177].

Looking at the overall composition of the surface as indicated by the percentage values in Table 7, it appears that the surface is enriched in oxygen as compared to the bulk. With S exposure, it is seen that the lower binding energy oxygen peak shifts to lower binding energies. The Fe 2p region shown in Figure 55 shows a band wide enough to include contributions from Fe in 4+ (712 eV) and 3+ (710 eV) oxidation states. With the exposure to S there is a very slight shift in peak positions, but there is no significant change in the Fe oxidation state. The
Co 2p region (Figure 56) showed a peak close to 781 eV associated with trivalent species. A value of 780.2 eV has been reported in the literature for La$_{0.4}$Sr$_{0.6}$Co$_{0.8}$Fe$_{0.2}$O$_3$ [132]. The shift towards slightly higher oxidation state could imply a small amount of tetravalent Co being present. With the exposure to sulfur, the surface composition of Co became too low and below the detection limit of the instrument.

Figure 52 Deconvoluted XPS spectra of La 4d region for LSCF 6428 with and without H$_2$S pre-treatment
Figure 53 Deconvoluted XPS spectra of Sr 3d region for LSCF 6428 with and without H₂S pre-treatment
Figure 54 Deconvoluted XPS spectra of O 1s region for LSCF 6428 with and without H$_2$S pre-treatment.
Figure 55 XPS spectra of Fe 2p region for LSCF 6428 with and without H₂S pre-treatment
Figure 56 XPS spectra of Co 2p region for LSCF 6428 with and without H₂S pre-treatment
Figure 57 Deconvoluted XPS spectra of S 2p region for LSCF 6428 with and without H₂S pre-treatment
Table 7  Peak positions and surface compositions calculated for deconvoluted XPS data for LSCF 6428 with and without H₂S pre-treatment.

<table>
<thead>
<tr>
<th>Region</th>
<th>Position (eV) no H₂S</th>
<th>500ppmH₂S</th>
<th>Surface Composition (%) no H₂S</th>
<th>500ppmH₂S</th>
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<tbody>
<tr>
<td>La 4d</td>
<td>103.8</td>
<td>102.5</td>
<td>2.2</td>
<td>3.4</td>
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<tr>
<td></td>
<td>101.2</td>
<td>100.0</td>
<td>4.7</td>
<td>3.0</td>
</tr>
<tr>
<td>Total</td>
<td>6.9</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr 3d</td>
<td>133.0</td>
<td>132.9</td>
<td>3.0</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>131.7</td>
<td>132.6</td>
<td>3.6</td>
<td>1.9</td>
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<tr>
<td></td>
<td></td>
<td>130.9</td>
<td></td>
<td>2.7</td>
</tr>
<tr>
<td>Total</td>
<td>6.6</td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co 2p</td>
<td>781.0</td>
<td>n/a</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>Fe 2p</td>
<td>710.3</td>
<td>709.3</td>
<td>12.1</td>
<td>8.5</td>
</tr>
<tr>
<td>O 1s</td>
<td>531.1</td>
<td>530.6</td>
<td>48.9</td>
<td>54.5</td>
</tr>
<tr>
<td></td>
<td>528.4</td>
<td>527.7</td>
<td>18.2</td>
<td>18.9</td>
</tr>
<tr>
<td>Total</td>
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<tr>
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<td>n/a</td>
<td>167.7</td>
<td></td>
<td>4.3</td>
</tr>
</tbody>
</table>

The XPS spectra show clear evidence of the adsorption of the sulfur on to the LSCF catalyst and the interactions with the catalyst. From the spectra, it is seen that the interactions are predominantly with the Sr and La species on the surface. No significant changes were observed in the Fe 2p region. In LSCF oxide materials, the Fe⁺³/Fe⁺⁴⁺ redox couple is known to play a dominant role in the oxidation activity[121, 135]. The relatively low interactions of the S with the Fe species could thus help explain the tolerance of the catalyst activity for methane oxidation to poisoning due to H₂S.
H₂S temperature programmed desorption (TPD) experiments were also conducted to study the adsorption-desorption characteristics over LSCF 6428. The catalyst was pretreated with 500ppm H₂S at 700°C for 5 hours. The TPD experiments were conducted in He and the results are shown in Figure 58. The m/z signals for the various desorbing species are plotted as a function of desorption temperature. Sulfur predominantly desorbs in the form of SO₂ (m/z = 64). The desorption takes place at high temperatures beyond the adsorption temperature. This implies that the sulfur species are stable on the catalyst surface at the lower temperatures. There is also some desorption of CO₂ (m/z = 44) possibly from atmospheric adsorption. The oxygen desorption signal (m/z = 32) is characteristic of the perovskites and has been observed previously in our TPD experiments [41].
7.2.2.c Discussion and Conclusions

The approach to develop novel sulfur and coke tolerant anodes has been a two-pronged approach. Modified cermet anodes were formulated and tested to look for synergistic effects of addition of another metal in preventing carbon formation as well as attack by sulfur. Oxide anodes were also studied and compared to the Ni-YSZ cermet in terms of activity and coking and sulfur tolerance. Addition of Cu and Sn to the Ni-YSZ was found to have a positive effect on reduction of carbon formation on the catalyst. The V-doped sample showed an increased carbon formation. However, the addition of Cu, Sn and V did not improve tolerance to sulfur poisoning. The LSCF 6428 perovskite oxide showed good promise in-terms of activity as well as tolerance to sulfur poisoning.
Stable conversions were observed and tested for up to 10hrs time on stream in the presence of 50ppm H₂S. Surface characterization of the sulfur-treated samples showed significant interactions of the surface Sr and La with sulfur and the presence of a surface sulfate group was detected. The catalytic activity in the perovskite oxide materials can be attributed to an interfacial mechanism, wherein the oxygen from the bulk plays an important role in oxidation of the surface species. The redox couples of the B-site transition metal ions help in the creation of oxygen vacancies and aid in mobility of the bulk oxygen to the surface for reaction as well as the transfer of the gas phase oxygen back into the bulk. The XPS spectra show very minimal interactions of the sulfur with the B-site cations, and helps explain the good sulfur tolerance observed over these catalysts. TPD experiment shows that the sulfur desorbs as SO₂ from the catalyst surface and hence reiterates the idea that the sulfur predominantly interacts in the form of surface sulfate species in the LSCF 6428 surface. These results show initial promise in using these materials as potential sulfur-tolerant anodes in SOFCs. Further testing of the catalysts in a button cell for electrochemical testing as well as testing for tolerance to other sulfur poisons including SO₂ and CS₂ is also important. Further long term deactivation testing is also necessary to establish the LSCF 6428 a good anode electrocatalyst.
CHAPTER 8. Conclusions

8.1 Cathode

The surface and bulk properties of La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_3$ formulations as a function of Sr concentration were evaluated. The oxygen vacancy generation capability as well as oxidation activity was found to be a strong function of the Sr content. Methane oxidation using oxygen as the limiting reactant was a useful probe reaction to study oxygen activation in these materials. Steady-state oxidation reactions were conducted and the oxygen activation energy was calculated as a function of Sr doping level using Arrhenius plots. While a Sr dopant level of 0.8 was found to be the most active in-terms of oxygen vacancy generation as well as oxygen and methane activation, TEC concerns need to be addressed by altering synthesis methods or including barrier layers to enable the use of this formulation as SOFC cathode materials.

Additional B-site doping with aliovalent transition metals such as Zn, Cu and Ni was studied to see the effect on oxygen transport and activation properties in LSCF catalysts. The addition of Zn to the B-site was found to significantly improve oxygen vacancy generation and activity. CO$_2$ TPO experiments were conducted to evaluate the oxygen activation and mobility in the catalyst. Methane oxidation experiments were conducted and activation energies
were found to be much lower with the LSCF-Zn sample. XAFS analysis of the catalysts helped in understanding vacancy generation and redox mechanisms at the B-site. The creation of oxygen vacancies at lower temperatures and lower activation energies for oxygen implied that this catalyst has the potential of being a successful cathode material especially for Intermediate temperature SOFCs.

8.2 Anode

The deactivation mechanism in Ni-YSZ was studied and the effect of water on the sulfur poisoning of the catalyst was explored. Oxidation sites were found to be less susceptible to attack by sulfur compared to methane reforming sites. TPD experiments showed that there were adsorption-desorption effects of H₂S on both the Ni as well as the YSZ surface, and these effects were more pronounced in the presence of water.

The new anode development studies followed a two-pronged approach wherein cermet materials as well oxide based anodes were studied for their activity and stability. With the addition of other metals to the Ni-YSZ, synergistic effects leading to reduction in coke formation were observed. However, issues of sulfur tolerance persisted, with the catalysts losing activity within 2 hours of exposure to 50ppm H₂S. With the oxide anodes, good activity for oxidation reactions were observed, and it was found that the carbon formation was very minimal even under oxygen-deficient feed conditions. The catalysts also showed tolerance to poisoning due to sulfur and maintained activity for up to 10 hrs on stream. Interactions of sulfur with the catalyst surface were studied through X-Ray Photoelectron Spectroscopy (XPS) and TPD studies. Sulfur was found to
predominantly interact with the La and Sr on the surface and surface sulfates were identified. It is likely that the redox couples in the B-site are not affected by sulfur and hence activity is maintained.
CHAPTER 9. Recommendations for future work

9.1 Cathode

Most of the cathode development work performed so far has focused on establishing and developing newer improved cathode formulations. There are many promising leads to explore based on the results presented. The catalyst formulations need to be tested under real fuel cell conditions. Electrochemical characterization of the catalysts is necessary to establish our new formulations as potential replacements for the state of the art LSM cathodes. More detailed quantification of the oxygen transfer properties is also necessary. There can also be more changes and optimization of the perovskite formulations aiming at improving long-term activity and stability as well as ease of fabrication.

9.1.1 Electrochemical testing

There is a lot of debate in the literature on the mechanism of oxygen activation in the mixed conduction oxide materials. It is assumed that both mass transfer and reduction kinetics, co-limit the performance [55-58]. Since electrochemical kinetic behavior has multiple factors influencing it, electrochemical impedance spectroscopy (EIS), also known as A.C impedance, is commonly used and is a powerful tool to determine the individual processes
involved, affecting performance in the electrodes and electrolyte. EIS has its advantage in that it is minimally invasive and can be used in systems in operation [178]. Using this technique, a sum of the electrolyte impedance, an interfacial impedance at medium frequency and a impedance associated with $O_2$ oxidation/reduction at the surface of the film can be obtained[8]. Impedance Spectroscopy is a useful technique to study the individual contributions to the overall cell polarization. The influence of the various governing physical and chemical processes in the system can be distinguished and studied qualitatively using this technique. This technique studies the response of a system to a small amplitude perturbation signal in terms of the relaxation times of the various dynamic processes in the system at different frequencies. It will help provide useful insights into the oxygen reduction mechanism and activity of the catalyst as well as help identify and quantify the various sources of electrochemical losses in the cell.

9.1.2 Button-cell development and testing

Button cell testing is the most common method for testing SOFC cells in a laboratory scale. Several steps in this process need to be optimized by trial and error as well by using suitable references from the literature. The sintering temperature, ink compositions, as well sealant materials used need to be optimized, and a standard protocol needs to be established for preparing the button cells.
9.1.2.a Barium-doped catalysts

There has been research suggesting that replacing the Sr in the A-site with Ba has shown initial promise especially for Intermediate Temperature SOFCs [52, 53]. Sr migration to the surface of the cathode layer causes significant problems with Cr poisoning [179]. The problems, associated with presence of Sr and chromium poisoning, make replacement with Ba a very attractive option. Characterization of these catalysts is necessary to quantify the oxygen content and baseline oxygen concentration of these catalysts better.

9.2 Anode

The anode work has identified important results in terms of understanding the interactions between H₂S and the Ni-YSZ surface. While it was observed that the oxidation sites were less susceptible to attack by sulfur than the sites involved in the methane decomposition and reforming routes, the exact nature of the sites has not been identified. Identifying the different types of sites on the Ni-YSZ catalyst and identifying those responsible and active for the anode oxidation steps will help in the design of better anode catalysts, as well as help discern the anode processes better. This is especially important for direct hydrocarbon feeds where a complicated network of reactions exists and sufficient knowledge about the nature of sites will help in tailoring the catalyst surface to minimize deactivation due to carbon formation as well as other poisons including sulfur. The characterization of the surface can be achieved through chemisorption and TPD experiments using probe molecules such as CO as well as methanol which has been successfully used for the cathode catalysts in our group before.
The oxide anodes have shown very good promise in terms of oxidation activity as well as resistance to coke formation and sulfur poisoning. The future work should involve more rigorous testing of the newer formulations. The most promising formulations should also be tested for electrochemical activity through single-cell testing, in conjunction with the cathode testing. While the initial assessment should be done using simple fuels such as $\text{H}_2$, electrochemical activity for oxidation of hydrocarbon fuels needs to be evaluated.

9.2.1 Transition metal-doped oxide catalysts

The oxide samples have shown very good promise as potential anode materials. However it was observed, that their catalytic activity for the various reforming reactions was very poor. Therefore modifications with additional metal loadings are necessary for improving their catalytic activity. Moreover these materials have very low surface areas and hence alternate preparation methods need to be looked into, to improve the surface area of these materials.

The LSCF materials can be modified, with additional transition metal doping on the A and B-site. Some of the formulations discussed in CHAPTER 5 can also be tested as potential anodes. Temperature programmed techniques that are used regularly in catalysis research, including reduction and oxidation profile testing can be employed to identify the active state and species in the catalysts. They will also provide insight into reducibility and redox stability of these catalysts which is important as the anode conditions are highly reducing in nature.
9.2.1.a Novel Synthesis techniques

There is a need to increase the surface area of the oxide catalysts in order to achieve higher conversions and better activity as well as stability. The current solid-state methods are simple and inexpensive ways to make perovskite oxide materials. However the high temperatures involved in this process result in sintering and hence large particle sizes, low porosity as well as very low surface areas. Our research group has expertise in organometallic synthesis methods as well as novel colloidal synthesis techniques that could be applied to these catalyst systems in order to improve surface area and tailor the particle size and orientation. BET studies based on the adsorption of Nitrogen/Krypton can be used to characterize the surface area and porosity of the catalyst. Particle size and morphology needs to be studied using TEM and X-Ray Diffraction. Pulsed chemisorption experiments with methanol as a probe molecule can be conducted to quantify and characterize the nature of the surface sites in these materials.

9.2.1.b XAFS and IR spectroscopy to study poisoning effects

X-ray absorption fine structure (XAFS) is a technique that is gaining much popularity in catalyst system studies due to the unique information that can be obtained from the technique using both \textit{in-situ} as well as \textit{ex-situ} experiments. Information about the nearest neighbors as well as inter-atomic distances and crystal coordination states can be obtained. The XANES (X-ray Absorbtion Near Edge Spectroscopy) region will give information about oxidation states. This technique will be extremely useful to study the perovskite oxides as a function of atmosphere and temperature as well as in an actual electrochemical cell. This
will provide a lot of useful information about the oxidation states of the B-site transition metals in the perovskites as well as about the oxygen content of the sample. This technique could also be used for deactivation studies to understand the catalyst interactions with sulfur and coke.

*In-situ* Infared spectroscopy of the catalysts is another useful method of studying the catalyst under actual fuel cell operation conditions. This technique will help understand the behavior of the catalyst surface under SOFC conditions better. Such surface behavior is the key to understanding activity and degradation mechanisms in SOFCs.
APPENDIX A: LIST OF ACRONYMS

DRIFTS – Diffuse Reflectance Infrared Fourier Transformation Spectroscopy
DSC – Differential Scanning Calorimetry
EXAFS - Extended X-ray Absorption Fine Structure
GC – Gas Chromatography
GDC – Gadolinium Doped Ceria
IT-SOFC – Intermediate Temperature Solid Oxide Fuel Cell
LSCF – Strontium and Cobalt doped Lanthanum Ferrite
LSM – Strontium Doped Lanthanum Manganite
MS – Mass Spectrometry
ORR – Oxygen Reduction Reaction
PEM – Polymer Electrolyte Membrane
SOFC – Solid Oxide Fuel Cells
TEM – Transmission Electron Microscopy
TGA – Thermogravimetric Analysis
TOF – Turnover Frequency
TPO – Temperature-Programmed Oxidation
TPR – Temperature-Programmed Reduction
TPRxn – Temperature-Programmed Reaction
WGS – Water-gas Shift
XAFS – X-ray Absorption Fine Structure
XANES – X-ray Absorption Near Edge Structure
XPS – X-ray Photoelectron Spectroscopy
XRD – X-ray Diffraction

YSZ – Yttria-Stabilized Zirconia
APPENDIX B – REACTION SYSTEM

H₂S → He → Ar → N₂ → CH₄ → H₂ → O₂ → Air

Mass flow Controllers

Bubbler

By-pass line

FURNACE

GC 2014
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