LSCF SYNTHESIS AND SYNGAS REACTIVITY OVER LSCF-MODIFIED Ni/YSZ ANODE

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LSCF SYNTHESIS AND SYNGAS REACTIVITY OVER LSCF-MODIFIED Ni/YSZ ANODE

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ABSTRACT

Simulated coal syngas reactivity over Ni/YSZ and LSCF (La\(0.6\)Sr\(0.4\)Co\(0.2\)Fe\(0.8\))-modified Ni/YSZ anode of SOFC (solid oxide fuel cell) was investigated in this study. The contribution of H\(_2\) and CO oxidation to total current density generation was determined from the electrochemical measurement and gas effluent analysis of the SOFC reactor. H\(_2\) oxidation was the dominant oxidation reaction over the Ni/YSZ anode reactions. Adding the LSCF on the Ni/YSZ anode increased the rate of CO oxidation, resulting in almost equal rate of H\(_2\) and CO oxidation. High oxidation rate of coke over LSCF-Ni/YSZ resulted in low carbon deposition on the anode surface. High oxidation rate of carbon was attributed to the high ionic conductivity of the LSCF which provided large amount of oxygen ions for fast oxidation of coke. LSCF was synthesized through the pechini method by replacing the standard calcination process with rapid combustion. Microstructure analysis, crystallography and resistivity measurement of the synthesized LSCF demonstrated similar properties to those of standard calcined LSCF. This result indicates that rapid combustion is a promising method for substitution of standard calcination process.
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I would like to dedicate this work to my family and fiancé, Ahmadreza, who have supported and helped me to this point in my life and beyond.
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1.1 Solid Oxide Fuel Cells, clean technology and renewable resources

Environmental concerns such as global warming and air pollution and the fact of our increasing demand to sustainable energy resources have been led to study and development of fuel cells which offer a clean technology to generate power at high efficiency. Using fuel cells as power generators decreases consumption of fossil fuels which cuts the oil import and eliminates the environmental problems such as air pollution, acidic rain, ozone depletion and radioactive emissions. Fuel cells also benefit from low operating and maintenance cost [1-3]. Fuel cells are classified based on their electrolyte; different types of fuel cells are listed in Table 1.1. Among different types of fuel cells, solid oxide fuel cells (SOFCs) attract a great interest due to the advantages over the traditional fuel cells
- high efficiency
- no need to noble metal catalysts (compared to polymer electrolyte and phosphoric acid fuel cells)
- high temperature exhaust which can be used for cogeneration
- fuel flexibility (a wide range of fuels can be used due to the high operating temperatures)
- solid electrolyte which does not have the corrosion and handling problems of liquid electrolyte
- very low NO\textsubscript{x} and SO\textsubscript{x} emission [3]
- long lifespan of 40000-80000 hours
- however, SOFCs suffer from these drawbacks
- high resistivity of electrolyte and polarization resistivity of electrodes
- solid state reaction at cathode/electrolyte interface which causes the formation of low conducting phase
- limitation for SOFC scale up due to the limited size of SOFC which is result of their ceramic material brittleness [1, 3-5]
Table 1.1 Characteristics of different types of fuel cells [1]

<table>
<thead>
<tr>
<th>FC type</th>
<th>Electrolyte</th>
<th>Catalyst</th>
<th>Fuel</th>
<th>Operating temp.</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali (AFC)</td>
<td>potassium hydroxide</td>
<td>platinum</td>
<td>H₂ or hydrazine</td>
<td>65-220°C</td>
<td>50-55%</td>
</tr>
<tr>
<td>Direct methanol (DMFC)</td>
<td>polymer</td>
<td>platinum</td>
<td>liquid methanol</td>
<td>60-200°C</td>
<td>40-55%</td>
</tr>
<tr>
<td>Phosphoric acid (PAFC)</td>
<td>phosphoric acid</td>
<td>platinum</td>
<td>H₂</td>
<td>160-210°C</td>
<td>40-50%</td>
</tr>
<tr>
<td>Proton-exchange</td>
<td>polymeric proton exchange membrane</td>
<td>platinum</td>
<td>H₂</td>
<td>40-80°C</td>
<td>40-50%</td>
</tr>
<tr>
<td>Molten carbonate (MCFC)</td>
<td>molten carbonate</td>
<td>electrode material</td>
<td>H₂, CO, natural gas or propane</td>
<td>630-650°C</td>
<td>50-60%</td>
</tr>
<tr>
<td>Solid oxide (SOFC)</td>
<td>ceramics and doped perovskites</td>
<td>electrode material</td>
<td>H₂, natural gas and hydrocarbons</td>
<td>600-1000°C</td>
<td>45-60%</td>
</tr>
</tbody>
</table>
High operating temperatures of SOFCs has advantages of rapid electrocatalysis without using noble metals, using of a wide range of fuels without any heat treatment and using high temperature exhaust of SOFC for cogeneration purposes. However, high operating temperatures limit the choice of materials for SOFC components and decrease the lifetime of SOFC [1, 6].

Effluent gasses vary with type of the fuels use for SOFCs. Using hydrogen as fuel produces water, heat and no greenhouse or acid gases; however hydrogen suffers from transportation and storage problems. Hydrocarbons benefits from more efficiency than H₂ and easier transportation and storage, but they result in formation of CO₂, CO and trace amounts of SOₓ and NOₓ. Since SOFCs are highly efficient, they use less amount of fuel to produce electricity compare to traditional thermal power plants; therefore, less amount of CO₂ and CO will be produced by SOFCs [1].

SOFCs have industrial, transportation and residential applications. SOFCs can be applied in computer, manufacturing and communication facilities due to their high power reliability and they can be used in urban areas because of their low emissions. Biological waste of industrial units can be used as fuel by SOFCs and waste heat generated by SOFCs can be employed by a heat engine, refrigerator or air conditioner [1, 7].

In this study coal syngas was applied as fuel for SOFC. Syngas is a gas mixture of varying amount of H₂ and CO which can be produced from coal gasification, biomass and steam reforming of natural gas or liquid hydrocarbons. Syngas with 50/50 ratio of the H₂ and CO can simulate the coal syngas with highest purity which produces from the coal gasification according to Eq.1.1. Simulated coal syngas was implemented as SOFC
fuel because of the abundance and low cost of the coal which makes it applicable for industry [8].

\[ C + H_2O \rightleftharpoons CO + H_2 \]  

(1.1)

1.2 Objectives and hypothesis

This study mainly consists of two parts, LSCF synthesis and SOFC testing. The objective of the first part is to develop a shortcut method for LSCF synthesis. The frequently used synthesis methods such as solid state reaction, citrate method, glycine-nitrate and EDTA titration require calcination at high temperature with a slow heating rate [9-15]. Calcination process is time and energy consuming, which prevents present methods become scaled up and industrialized. Therefore, the objective is to replace calcination process with a rapid combustion process to consume less time and energy for preparation of LSCF perovskite. The objective will be achieved via direct combustion of LSCF precursor for a short period of time. The hypothesis is that the crystalline pure perovskite phase of LSCF with high porosity and high electrical conductivity could be formed by rapid combustion of the LSCF precursor for certain combustion duration.

The second part is a study of electrochemical reactions and products and the objective is to test the cells in simulated coal syngas (H$_2$/CO) in order to determine the contribution of H$_2$ and CO oxidation to total current density generation of the SOFC. The behavior of typical Ni-based anodes in syngas is similar to that in H$_2$ and oxidation of H$_2$ is the dominant reaction for current generation [16-17]. In this study synthesized LSCF was added to the Ni anode by screen printing a thin layer of LSCF on the Ni anode.
surface and the hypothesis is that LSCF cause changes in contribution of H\textsubscript{2} and CO oxidation to total current density generation.

1.3 Outline

Chapter I provides an introduction on energy resources, consumption and environmental problem consequences. SOFC was introduced as a clean technology and renewable resources and was compared to the other types of fuel cells. Objectives and hypothesis of the study were described at the end of the chapter. Chapter II presents information about SOFC components, properties and principles along with H\textsubscript{2}/CO oxidation on SOFC anodes. Information about perovskite materials, their synthesis and properties are also provided in this chapter. Chapter III explains the experimental procedure from LSCF synthesis to SOFC testing. Chapter IV contains results and discussion of the LSCF powder characterization and electrochemical performance of the cells in coal syngas. It also presents the data for calculation of molar concentration for reactants and products and contribution of each reaction in current density generation. Chapter V describes the findings and conclusion of this study.
CHAPTER II
BACKGROUND

2.1 Solid Oxide Fuel Cell (SOFC)

Solid oxide fuel cells can be defined as ceramic multilayer structures which directly convert the electrochemical energy into electrical energy using a fuel and an oxidant. A solid oxide fuel cell consists of two porous electrodes which are made of transition metal oxide materials and a dense layer of oxygen ion conducting solid oxide electrolyte which separates the positive and negative electrodes. Components of SOFC must indicate thermo-mechanical stability at high operating temperatures (typically 650-1000 °C), thermal and chemical compatibility with one another and good adhesion at the electrode/electrolyte interfaces. Performance of a SOFC is affected by intrinsic materials properties, fabrication technologies and operating conditions. Electrolyte of the SOFC is a dense layer which let the oxygen ions pass through at high operating temperatures of SOFC while it is gas tight and electrically non-conductive. Electrodes are porous conductive materials which enable the transport of gaseous compounds and electrons. The most common electrolyte, cathode (positive electrode) and anode (negative electrode) materials are yttria statbilized zirconia (YSZ), lanthanum strontium manganite oxide (LSM) and nickel cermet, respectively [3, 5]. Fuel cells and batteries operate based
on similar principles, but fuel cells do not require charging and they continue operating as long as fuel and oxidant are provided [1]. SOFCs operate by redox reactions of the oxygen molecules and fuel on the three phase boundary (i.e. electrolyte, electrode and current collector interface) [7]. Cathode is exposed to the air and the oxygen molecules from the air adsorb on its surface and combine with the electrons coming through the external circuit to form oxide ions (eq. 2.1). These oxide ions diffuse into the anode through the electrolyte and react with the fuel (H₂, for example) to produce water and deliver electrons according to eq.2.2. Electrons move from anode to the cathode via an external circuit to complete the electrochemical cycle [18].

\[
\begin{align*}
1/2O_2(g) + 2 e^- & \rightarrow O^2_-(s) \quad (2.1) \\
O^2_-(s) + H_2(g) & \rightarrow H_2O(g) + 2e^- \quad (2.2)
\end{align*}
\]

Cathode materials have to show high catalytic activity, stability and electrical conductivity whereas comprising a porous structure. LSM shows ionic conductivity due to the oxygen deficiency or excess of perovskite structure and exhibits high electrical conductivity because of hopping of an electron hole between the Mn⁺³ and Mn⁺⁴ while taking advantage of doped strontium. Electrolyte of SOFC is a non-electrical conductive but O²⁻ ionic conductive layer which enables the oxide ions transport from the cathode to the anode side. Y₂O₃ provides oxygen vacancies in YSZ structure which results in oxide ions conducting property of YSZ according to the eq.2.3 (from Kroger–Vink notation [19]):

\[
Y_2O_3 (ZrO_2) \rightarrow 2Y^\cdot Zr + 3O^\cdot_o + V^\cdot_o \quad (2.3)
\]

where \(V^\cdot_o\) stand for oxide ion vacancy and \(O^\cdot_o\) represents oxide ion in the crystal lattice of the electrolyte. In addition to O²⁻ ionic conductivity, electrolyte of SOFC should be a
dense and thin layer to prevent gaseous compounds transport and minimize the ohmic resistivity of the cell [3, 20].

Anode of SOFC is a porous catalytic active and electrical conductive material which is stable at reducing environment of the anode side. Nickel is a good candidate for this purpose but nickel particles sinter at high operating temperatures of the SOFC and form a less porous structure which causes difficulty in transportation of gaseous reactants and products. To avoid sintering of nickel particles, nickel and YSZ are mixed together and form Ni/YSZ cermet (ceramic-metallic) in which YSZ surrounds the Ni particles. Ni/YSZ layer shows a closer thermal expansion coefficient to the YSZ electrolyte and a better adhesion to the electrolyte surface. Mixing with YSZ can also be applied for the LSM to make a cathode interlayer which benefits from a better adhesion to the electrolyte surface [3]. According to Eq. 2.2 H$_2$ molecules get oxidized and release two electrons which generate an open circuit voltage of 1.055 V at 800 °C.

2.2 Electrochemical properties of SOFC

Voltage-current characteristic measurements and Electrochemical Impedance Spectroscopy (EIS) are two major techniques for electrochemical analysis of the solid oxide fuel cells.

Voltage-current polarization curves are the most frequently used technique to determine the voltage and current of a solid oxide fuel cell. In an open circuit (i.e. no current is flowing through the circuit) the cell potential is close to the reversible potential (Nernst potential) which is expressed by Eq.2.4
\[ V_{\text{Nernst}} = \frac{-\Delta G}{n_e F} = \frac{-\Delta G^0}{n_e F} - \frac{R_g T}{n_e F} \ln\left[ \prod_i (p_i^0)^{\eta_i} \right] \] (2.4)

where \( F \) is the Faraday’s constant, \( R_g \) is the universal gas constant, \( T \) is the operating temperature and \( p_i \) is the partial pressure of the gases in the bulk flow. When the current flows, voltage decreases due to the losses resulting from irreversibility. Voltage loss includes ohmic, activation and concentration losses. Ohmic loss resulted from the resistances through the path of electrical charges which are associated with cathode, anode, electrolyte, interconnectors and current collectors and it is usually a function of temperature [21]. Activation polarization associated with the irreversibilities of electrochemical reaction which is defined by Butler-Volmer equation

\[ i = i_0 \left[ \exp \left( \alpha \frac{n_e F}{R_g T} \eta_{\text{act}} \right) - \exp \left( -(1 - \alpha) \frac{n_e F}{R_g T} \eta_{\text{act}} \right) \right] \] (2.5)

where \( i \) is the current density, \( i_0 \) is the exchange current density, \( \alpha \) is apparent charge transfer-coefficient and \( \eta_{\text{act}} \) stands for activation polarization. Concentration loss occurs due to the diffusion phenomenon which results in concentration difference between the gases of the electrochemical reaction and bulk flow of the gases. Two different ways of diffusion take place for each electrode: (i) external diffusion, in the boundary layer of the electrode and bulk of the gases (ii) internal diffusion, between the porous structure of the electrodes and reaction sites. Therefore, the ‘true’ reversible cell potential is calculated from Eq.2.6

\[ V_{\text{Nernst}} = \frac{-\Delta G}{n_e F} = \frac{-\Delta G^0}{n_e F} - \frac{R_g T}{n_e F} \ln\left[ \prod_i (p_i^0)^{\eta_i} \right] \] (2.6)
where $p_i^*$ is the partial pressure of the gaseous species at the reaction sites. Therefore, voltage deviation from the theoretical thermodynamic value is equal to the difference between Eq.2.4 and 2.6 due to the concentration loss [22].

2.3 Oxidation of H$_2$ and CO

Electrochemical oxidation of H$_2$ on the Ni-based anodes consists of a multistep mechanism including the (i) H$_2$ adsorption on the anode surface, (ii) diffusion of the H or H$^+$ ion to the triple phase boundary (TPB), (iii) ionization of surface H atom, (iv) charge-transfer reactions of H$^+$ with O$^{2-}$ and OH$^-$ ions at the TPB, and (v) desorption of the H$_2$O molecules form the surface. Electrochemical oxidation of CO on the Ni anode surface occurs through a multistep mechanism including (i) adsorption of CO on the anode surface, (ii) O$^{2-}$ transfer to the TPB, (iii) charge-transfer reactions with O$^{2-}$ at the TPB, and (iv) dissociation of the produced CO$_2$ from the anode surface. The overall oxidation process is similar for H$_2$ and CO; however there is a difference in step (i) for adsorption mechanism of H$_2$ and CO. The adsorption mechanism of the H$_2$ molecules on the anode surface is dissociative while it is nondissociative for the CO adsorption [16].

2.4 Perovskites oxides for SOFC components

Perovskite is a type of mixed oxides having two or more different cations with different ionic radii, valences and coordination numbers. The most typical formula for perovskite material is ABO$_3$ in which A and B are two different metal cations. Different
A and B atoms form different crystal structures such as cubic, tetragonal, orthorhombic and rhombohedral which result in different properties. The ABO$_3$ perovskite with a cubic lattice is shown in Figure 2.1. Perovskite-type oxides have been studied as SOFC components because of their variety in structures and compositions, thermal and chemical stability and mixed conducting property. Among different perovskite oxides, Mn and Co based oxides have been commonly applied in SOFC electrodes due to the high catalytic activity and ionic-electronic conductivity [23]. Mn and Co based perovskites are used in this study as the cathode and anode materials, respectively.

![Cubic crystalline structure of perovskite oxide](image)

Figure 2.1 Cubic crystalline structure of perovskite oxide

2.4.1 Ionic-electronic conductivity

A and B metal cations in perovskite oxides with general formula of ABO$_3$ can be substituted by another cation M with similar size but higher/lower oxidation state than
that of A or B which causes oxygen excess/vacancy in the crystal structure and results in higher ionic conduction. Oxide ions transportation is facilitated using the oxygen vacancies in $A_{1-x}M_xBO_3-\alpha$ or $AB_{1-x}M_xO_3-\alpha$ when the energy for the oxide ions to jump from their original spot to the vacant site is not too high. The concentration and the size of the dopants are effective factors on oxide ion conductivity. Oxide ion conductivity increases with higher concentration of dopants and reaches to an optimum value; above that point increasing the amount of dopant results in formation of dopant and vacancy cluster which decreases the oxide ion conductivity. Dopants with ionic radii close to that of host cations result in higher ionic conductivity and increasing the ionic radii of dopants decreases the conductivity. Perovskite materials benefits from mixed conducting property under oxidizing atmosphere at elevated temperatures. Hole conduction generates via the defect equilibrium with oxygen in gas phase as shown in Eq. 2.7 which results in electronic conductivity.

$$V_O + \frac{1}{2} O_2 \rightleftharpoons O_{O}^x + 2h$$

(2.7)

Hole conduction takes place even in weak oxidizing atmospheres such as air for many of the perovskites due to their large equilibrium constant for Eq. 2.7. Doping another metal cation in perovskite structure increases the electrical conductivity with increasing the number of charge carries (holes). Perovskite materials such as $La_{1-x}Sr_xMnO_3$ (LSM, La is doped with Sr) and $La_{1-x}Sr_xCo_{1-x}Fe_xO_{3+\delta}$ (LSCF, La and Co are doped with Sr and Fe, respectively) exhibit high mixed conductivity (ionic-electronic conductivity). A and B doped cations comprising oxygen vacancies and first-row transition metal elements
possessing multi-valency under different conditions result in high ionic and electronic conductivity, respectively [23].

2.4.2 Catalytic activity

As mentioned before, cathode and anode material must indicate high catalytic activity to adsorb and dissociate the gas species. Cathode catalyst adsorbs the oxygen molecules on the surface, dissociates and charges them. Among various types of materials, perovskites showed high catalytic activity for oxygen reduction reaction due to the high surface activity to oxygen reduction ratio resulting from the large amount of oxygen vacancies. In-situ techniques such as IR spectroscopy were applied to study the cathode reaction mechanism based on the adsorbed species on the surface [23-25].

2.4.3 Stability and compatibility

Cathode and anode materials for SOFC must show thermal and chemical stability and compatibility at high operating temperature in contact with electrolyte. On the cathode side during the SOFC operation current flow causes an oxygen flux on the electrode-electrolyte interface which results in disequilibrium with gas phase. This can force the cations to move from electrode-electrolyte interface side to gas phase side which causes the changes in microstructure of the cathode. The cation diffusivity must be low for electrode materials to maintain the microstructure during the long-term operations. Another factor for cathode materials is chemically lattice expansion due to
the formation of oxygen vacancy in the cathode structure. Thermal or chemical expansion changes the structure of cathode and anode materials from the fabrication state. A proper electrode material can be applied to minimize the thermal and chemical expansion by considering the thermal expansion coefficient and oxygen vacancy [23, 26].

2.4.4 Synthesis methods

Perovskite-type oxides which have been used for SOFC components exhibit thermal and chemical stability, mixed conducting property and also high catalytic activity at operation temperatures of SOFC. Preparation method of perovskite is a determining step to achieve these requirements. Different synthesis methods result in different structures and particles sizes which lead to different properties. Various synthesis methods have been implemented to prepare the perovskite oxides for SOFC purposes, among them Pechini method was one the most successful techniques. Other synthesis approaches such as solid state reaction [13, 27-28], glycine-nitrate method [14-15, 29] and spray pyrolysis [30] have been applied in several studies. Pechini method is implemented in this study which is described in detailed later in section 3.1.
CHAPTER III
EXPERIMENTAL

3.1 LSCF powder preparation

The La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$ (LSCF) anode powders were prepared by Pechini method as shown in Figure 3.1 [31][11, 32-34]. Metal nitrates of La, Sr, Co and Fe (La(NO$_3$)$_3$.6H$_2$O, Sr(NO$_3$)$_2$, Co(NO$_3$)$_2$.6H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O from Alfa Aesar) with a molar ratio of 3:2:1:4 were dissolved in deionized water at room temperature. Citric acid (BDH) with C/M ratio (i.e. molar percentage of citric acid to all metal cations) of 1.5 and ethylene glycol (Sigma, USA) were added to the aqueous solution under heating and stirring to bind the metal cations and form a brownish gel. The produced gel was divided into two portions, one portion was calcined at 700°C for 2 h with heating rate of 5°C/min, and the other part was combusted for certain period of time (2, 3 and 4 minutes) using a torch to yield a black powder. The synthesized LSCF powders were characterized using X-ray diffractometer (XRD, Cu Kα radiation), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) and resistivity measurement. The results compared with those of commercial LSCF powders (from FCM).
Figure 3.1 Flow chart of the pechini method procedure for LSCF perovkite synthesis
3.2 Cell fabrication

This section describes the procedures applied for fabrication of anode supported fuel cells for this study along with the materials and equipments which have been used to make the fuel cells.

3.2.1 Fabrication of anode-supported fuel cell

Disk-shaped anode-supported fuel cell in this study consists of an anode support, anode interlayer, electrolyte, cathode interlayer, and cathode. The anode support, anode interlayer and electrolyte were prepared by co-casting the slips using a doctor blade, followed by drying at room temperature. The slips were prepared from dispersing the Yttria Stabilized Zirconia (YSZ, TZ-8Y Tosoh), and Nickel oxide (NiO, Atlantic Equipment Engineers) powders in organic solvents, followed by adding the binder, plasticizer and pore-former to the mixture and ball milling for 24 h. Anode support, anode interlayer and electrolyte contained NiO/YSZ 70/30 wt%, NiO/YSZ 60/40 and pure YSZ, respectively. Green tape (dried co-casted slips) was cut into disk shapes using a laser cutter and resulting disks were fired at 1000˚C for 16 h and at 1400˚C for 2 h. The cathode interlayer, LSM/YSZ 70/30 wt% (Heraeus), and cathode, pure LSM (Heraeus), were screen printed on the electrolyte side of the fuel cells and sintered at 1250˚C and 1100˚C for 2 h, respectively.
3.2.2 LSCF anode preparation

The LSCF anode pastes were prepared by mixing the commercial, calcined and combusted LSCF powders with terpineol, binder and dispersant reagents at 50\% of solid content and ball milling for 48 h. The paste was screen printed on the anode side of the cell followed by a sintering at 1200°C for 2 h. Another layer of paste was applied on the first layer and was sintered.

3.3 SOFC testing

The experimental apparatus is illustrated in Figure 3.2 including gas flow metering system, SOFC reactor and current collectors, effluent gas analysis and electrochemical analysis systems.
3.3.1 Gas flow metering

The gas flow metering system was designed to control and deliver gas flows to the SOFC reactor. Mass flow controllers were used to adjust the flow rates of He, H₂ and CO to deliver 100 sccm stream of He/H₂ 50/50 vol%, He/CO 50/50 vol% and He/H₂/CO 50/25/25 vol%.

3.3.2 Reactor and current collector

The SOFC reactor is a rimed steel tube which also serves as the anode current collector equipped with gas inlet and outlet tubes. To start the fuel cell assembly, a thin
layer of silver paste (Heraeus) was coated on the rim of the reactor to enhance the contact between the anode surface and the steel reactor. Fuel cell was placed on the rim and was sealed to the reactor with the aid of a ceramic seal (Cotronics). Cathode current collector consists of a silver paste on the cathode surface and a silver strip to pull out the current which was fixed on the cathode using a piece of mica as an insulator. Fuel cell was placed into the furnace and heated to 800°C at a heating rate of 3°C/min with a stream of He/H₂ (100 sccm, 50 vol% H₂).

3.3.3 Effluent gas analysis

A quadrupole mass spectrometer was used to analyze the gas effluent. The outlet of the reactor was connected to the mass spectrometer during the experiment, and mass spectrometer was connected to a personal computer to monitor the gas species. For all of the experiments, the vacuum chamber of the mass spectrometer was operated at $5 \times 10^{-6}$ mbar.

3.3.4 Electrochemical analysis

Voltage-current polarization curves are the most common approach to determine the voltage and current of a solid oxide fuel cell. In an open circuit (i.e. no current is flowing through the circuit) the cell potential reaches to a maximum value which is close to the reversible potential (Nernst potential, Eq.2.4). When the current flows through the circuit the voltage decreases and it reaches approximately to zero at the maximum load.
current. Power density which is usually a representative of the cell performance can be obtained from every single data point of voltage-current polarization. Voltage-current measurement was performed at 800°C with 100 sccm of He/H₂ (50 vol% H₂), He/CO (50 vol% CO) and He/H₂/CO (25 vol% H₂, 25 vol% CO) on the anode side while the cathode side was exposed to the air. The fixed-voltage test was carried out at a constant voltage of 400 and 1 mV at 800°C with gas flows similar to voltage-current measurement. The anode was reduced at 800°C with a stream of He/H₂ (100 sccm, 50 vol% H₂) before the electrochemical measurements.

Electrochemical impedance spectroscopy was applied to measure the fuel cell resistance at the operating temperatures. The impedance measurements were carried out in a frequency range of 1 MHz to 100 mHz at three DC current of 0 mA/cm², medium and maximum current densities of the fuel cell. All of the electrochemical measurements were conducted using a Solartron 1400 CellTest System (Appendix A).

3.4 Experimental procedure

The overall experimental procedure is demonstrated in Figure 3.3. The experiment 1 was designed to determine the baseline performance of the Ni/YSZ anode supported fuel cell (Ni fuel cell) using the syngas as fuel and compare the results with those of LSCF/Ni/YSZ anode supported fuel cell (LSCF/Ni fuel cell). The experiment 1 was started with reducing the cell in a stream of He/H₂ (100 sccm, 50 vol% H₂) at 800 °C followed by switching the stream to 100 sccm of He to eliminate the H₂. CO was flowed to the reactor when no H₂ was observed in
mass spectrometry results of effluent gas. The cell continued operating in 100 sccm of He/CO (50 vol% CO) at 800 °C. The gas stream was switched to He/H₂/CO (25 vol% H₂ and 25 vol% CO) when the current became stable under a load of 400 mV. Figure 3.4 shows the diagram of changing the flow rates during the experiment. Voltage-current and AC impedance measurement were carried out for all three steps of the experiment. Step changes were applied on the fuel cell with a sequence of OCV (open circuit voltage) condition, 1 mV load and 400 mV load each for 1 h using the syngas as fuel. Voltage, current and effluent gas were monitored and recorded during the step changes in order to quantify the products under different conditions and determine the contribution of H₂ and CO oxidation to total current density generation. The experiment 2 was started with reducing a LSCF/Ni fuel cell in a stream of He/H₂ (100 sccm, 50 vol% H₂) at 800 °C and it followed similar sequences as experiment 1. The fuel cells continued operating in syngas at 800 °C until they degraded due to the coking on the anode surface.
Figure 3.3 Flow chart of the fuel cell testing procedure

Experiment 1

Ni fuel cell

Reducing in H₂ at 800 °C

Operating in CO at 800 °C

Operating in CO/H₂ at 800 °C

OCV - 1 mV - 400 mV step changes in CO/H₂ at 800 °C

Experiment 2

LSCF-Ni fuel cell
Figure 3.4 Schematic of the fuel cell testing at 800°C switching from He+H₂ (100 sccm, 50 vol% H₂), to He+CO (100 sccm, 50 vol% CO), and to He+H₂/CO (100 sccm, 25/25 vol% H₂/CO)
CHAPTER IV
RESULTS AND DISCUSSION

4.1 LSCF powder characterization

Different characterization techniques including XRD, SEM, EDX and resistivity measurement were applied to characterize and compare the result of the combusted, calcined and commercial LSCF powders. Another comparison was performed between combusted LSCF powders which were combusted for different periods of time, 2, 3 and 4 minutes.

4.1.1 XRD crystallography of LSCF powders

Figure 4.1 shows the XRD patterns of the combusted, calcined and commercial LSCF powders. All three powders show the rhombohedral structure with no impurity phase [10-11, 35-37]. XRD result of combusted LSCF suggests that rapid combustion method produced a pure perovskite phase of LSCF similar to that of LSCF obtained from calcination at 700°C. Figure 4.2 shows the XRD pattern of the LSCFs, which were combusted at different periods of time. The pattern of LSCF which was combusted for 2
min reveals an impurity peak of Co$_2$O$_3$ and this peak was disappeared after extending the combustion duration to 3 min.

Figure 4.1 XRD patterns of combusted (for 3 min), calcined and commercial LSCF powders – filled circle indicates characteristic peaks of rhombohedral LSCF perovskite
Figure 4.2 XRD patterns of combusted LSCF powders

4.1.2 Microstructure analysis of LSCF powders

Figure 4.3a,b shows the SEM micrographs of the LSCF perovskite oxides prepared by the pechini method and then combusted/calcined. The mean particle size is in micro scale, between 1 to 5 µm for the combusted and between 10-30 µm for the calcined powder. Figure 4.4 shows the SEM images of the sintered LSCF on the anode side of the cells. After sintering the particle size became about five times smaller and a smaller amount of agglomerated particles is observed for sintered LSCFs. A more even
distribution can be observed for the sintered-combusted LSCF (Figure 4.4 a) than that of the sintered-calcined LSCF (Figure 4.4 b).

Figure 4.5 a-c shows the SEM micrographs of the porous LSCF powders combusted for different periods of time, 2, 3 and 4 min.

Figure 4.3 SEM micrographs of LSCF powders synthesized by the pechini method and (a) combusted for 3 min and (b) calcined at 700°C for 2 h

Figure 4.4 SEM micrographs of LSCFs, top layer of the LSCF-Ni/YSZ anode of the cell synthesized by the pechini method and (a) combusted for 3 min and sintered at 1200°C for 2 h; (b) calcined at 700°C for 2 h and sintered at 1200°C for 2 h
Figure 4.5 SEM micrographs of LSCF powders synthesized by the pechini method and then combusted for (a) 2 min, (b) 3 min and (c) 4 min

4.1.3 Resistivity measurement

LSCF powders were pressed to make a pellet in order to measure the resistivity. Resistivity of the combusted and calcined LSCF pellets was measured using a potentiometer at a distance of 1 cm on the pellet surface. Resistivity values are reported in Table 4.1. Combusted LSCF powders were combusted at different periods of time, 2, 3 and 4 minutes. Resistivity of LSCFs with different combustion durations shows the order of 4 min > 2 min > 3 min which suggests an optimum value for the combustion
duration close to 3 min resulted in the highest electrical conductivity (reciprocal of resistivity). Combusting the LSCF for 2 min was not enough to form good necking features between the particles to create high electrical conductivity; therefore, the combustion duration was increased to make strong bonding between the particles. The electrical conductivity increased with combustion duration from 2 to 3 min and showed an optimum value close to 3 min, followed by a decrease of electrical conductivity with longer combustion duration. This can be attributed to an increase in the amount of liquid when the combustion duration was long, which resulted in formation of an amorphous phase and dense regions in the bulk consequently decreased the electrical conductivity [9]. The calcined LSCF showed a higher resistivity than that of LSCF combusted for 3 min, but the resistivity was lower than those of LSCF combusted for 2 and 4 min.

Table 4.1 Resistivity values of combusted (with different combustion durations) and calcined LSCFs

<table>
<thead>
<tr>
<th>Type of LSCF</th>
<th>Resistivity (Ω.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined</td>
<td>700</td>
</tr>
<tr>
<td>Combusted 2 min</td>
<td>1000</td>
</tr>
<tr>
<td>Combusted 3 min</td>
<td>600</td>
</tr>
<tr>
<td>Combusted 4 min</td>
<td>1400</td>
</tr>
</tbody>
</table>

4.2 Electrochemical and microstructure analysis of the Ni fuel cell

The first part of this section describes the electrochemical performance including the voltage-current characteristics and, electrochemical impedance spectra and current density measurement at fixed voltage of the cell with a Ni/YSZ anode. The second part
provides the data of microstructure analysis including SEM, EDX and mapping of the cell after the test.

4.2.1 Voltage-current characteristics

Figure 4.6 shows the voltage-current polarization curves of the cell with a Ni/YSZ anode operating at 800°C in He+H₂, He+CO, and He+H₂/CO fuels. The OCV (open circuit voltage) and power density vary with the type of fuel, indicating an order of H₂ > H₂/CO > CO. The cell showed a maximum current density of 503, 461 and 500 mA/cm² and a maximum power density of 110, 84 and 98 mW/cm² in H₂, CO and H₂/CO, respectively. The lowest performance of the cell in CO could be attributed to the slower rate of CO oxidation than the rate of H₂ oxidation, the low effective diffusivity CO and its higher activation polarization [17]. It could also result from the disproportionation of CO according to Eq.4.1 taking into account that Ni is an active catalyst for dissociation of CO to carbon. Carbon species could decrease the cell performance by deposition on the anode surface [38].

\[
2\text{CO} \rightarrow \text{CO}_2 + \text{C} \quad (4.1)
\]

Current density of the cell in H₂/CO (syngas) is similar to that in H₂, indicating that the Ni anode in H₂/CO performs similar to that in H₂. This result may suggest that in a mixture of H₂ and CO, the H₂ oxidation is the dominant oxidation reaction with the Ni anode. The water gas shift reaction, Eq.4.2, could also play a role in improving cell performance by shifting CO to CO₂, resulting in less CO for direct electrochemical oxidation to CO₂, for which activation polarization is high[17]. Generally the oxidation
reaction of H$_2$ to H$_2$O demonstrates a higher current density and lower anodic overpotential than the oxidation reaction of CO to CO$_2$ on Ni anodes [8, 16].

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$$  \hspace{1cm} (4.2)

Figure 4.6 V-I curves of the cell with Ni/YSZ anode at 800°C in (▲) He+H$_2$, 100 sccm, 50 vol% H$_2$; (■) He+CO, 100 sccm, 50 vol% CO; and (●) He+H$_2$/CO, 100 sccm, 25/25 vol% H$_2$/CO

4.2.2 Step changes of voltage and current

Figure 4.7 shows the MS intensity of the exhaust gas of the reactor along with the voltage and current density profiles of the cell with the Ni/YSZ anode. Step changes in the current and voltage were applied on the cell to monitor the gas exhaust of the reactor using mass spectroscopy to quantify the amount of electrochemical reaction products at
each step with different voltages and currents. The first step of the experiment was performed at OCV (i.e. no current was flowing through the circuit) for 20 minutes and the voltage was recorded. The experiment was followed by recording the current at a constant voltage of 1 mV for another 20 minutes. In the third step, the voltage was changed to 400 mV for the last 20 minutes and the current was recorded. The gas exhaust was recorded using the MS during the experiment. The first step showed a stable open circuit voltage of 0.94 V and the MS intensity of H₂ and CO with a m/e ratio of 2 and 29 (28 also represents CO but it has overlapping with other species) showed their maximum values. Since the current was zero and no oxygen ion was flowing from the cathode to the anode side, no oxidation reaction of the fuels occurred. Consequently the MS intensity of the oxidation reaction products including H₂O and CO₂ with a m/e ratio of 18 and 44 indicated their minimum values at OCV. After 20 minutes the condition switched to the constant voltage of 1 mV, which is very close to zero and results in the highest current density and highest oxygen ion concentration. The current density showed a maximum value of 510 mA/cm² and it decreased to 460 mA/cm² by the time passed. The trend of the current density could be a result of the sudden change of the condition, which suddenly introduced a high amount of oxygen ions to the anode and resulted in a high current density and the current density became stable as the time passed. The MS intensity of H₂ and CO was the lowest at 1 mV, which demonstrates a high consumption of the fuels due to the high concentration of oxygen ions at the high current density. Therefore, the MS intensity of H₂O and CO₂ showed its maximum value at a constant voltage of 1 mV. In the third step, the voltage was switched from 1 mV to 400 mV, which decreased the current density from 460 to 250 mA/cm². The current
density was stable and it showed a small fluctuation between 250 and 240 mA/cm$^2$. The MS intensity of the reactants and products was in between the MS intensity at the first and the second step of the experiment. The applied voltage on the cell was lower than the previous step, resulting in a lower current density and a lower oxygen ion concentration, which consumed a less amount of H$_2$ and CO to produce H$_2$O and CO$_2$. Molar concentrations of the reactants and products of the electrochemical reactions during the step changes were calculated from the MS intensities and current density to determine the contribution of each reaction to the overall electrochemical performance of the cell. The results of the molar calculation will be presented in section 4.4.
Figure 4.7 Graph (a) MS intensity of the exhaust gas of the reactor (b) voltage and (c) current density profile at OCV, 1 and 400 mV of the cell with Ni/YSZ anode at 800°C in He+ CO/H₂ during the step changes of voltage.
4.2.3 Microstructure analysis of the Ni fuel cell

Figure 4.8 shows the SEM image of the Ni anode surface along with the EDX composition profile. The SEM image shows an even distribution of Ni particles surrounded by YSZ. EDX indicates peaks of Ni, Zr, Y and O of the anode along with the carbon peak which could evidence the deposition of carbon on the Ni anode surface.

Figure 4.9 shows the SEM, EDX and mapping elemental analysis for the cross section of the cell with a Ni/YSZ anode. Carbon mapping of the cross section with a higher density of carbon on the external anode surface and the carbon peak in the EDX data evidence the deposition of carbon on the Ni anode surface. In addition to Ni, Zr, Y, O and C, peaks of La, Sr and Mn are also appeared in the EDX data, which represent the composition of the LSM cathode.
Figure 4.8 Result of microstructure analysis (a) SEM micrograph (b) EDX of the anode surface of Ni fuel cell
4.3 Electrochemical and microstructure analysis of the LSCF-Ni fuel cell

The first part of this section presents the data of the electrochemical performance including the voltage-current characteristics and, electrochemical impedance spectra and current density measurement at a fixed voltage of the cell with the LSCF-Ni/YSZ anode. The second part provides the results of microstructure analysis including SEM, EDX and mapping of the cell after the test.
4.3.1 Voltage-current characteristics

Figure 4.10 shows voltage-current polarization curves of the cell with the LSCF-Ni/YSZ anode operating at 800°C in He+H₂, He+CO, and He+H₂/CO as fuel. The OCV and power density vary with the type of fuel, indicating an order of H₂ > H₂/CO > CO. The cell showed a maximum current density of 610, 545 and 575 mA/cm² and a maximum power density of 117, 96 and 109 mW/cm² in H₂, CO and H₂/CO, respectively. The lowest performance of the cell in CO can be resulted from the slower rate of CO oxidation than the rate of H₂ oxidation. Current density of the cell in H₂/CO (syngas), 575 mA/cm², is nearly equal to the average of the current densities in H₂, 610 mA/cm², and in CO, 545 mA/cm², indicating that the electrochemical performance of the LSCF-Ni anode in H₂/CO is in between the performance of that in H₂ and that in CO. This observation may suggest that in a mixture of H₂ and CO, neither H₂ oxidation nor CO oxidation is the dominant oxidation reaction with the LSCF-Ni anode and these two reactions could proceed in parallel.
4.3.2 Step changes of voltage and current

Figure 4.11 shows the MS intensity of the exhaust gas of the reactor along with the voltage and current density profile of the cell with the LSCF-Ni/YSZ anode. Step changes in the current and voltage were applied on the cell monitoring the gas exhaust of the reactor by mass spectroscopy to quantify the amount of electrochemical reaction products at each step with different voltages and currents. The first step of the experiment was performed at OCV (i.e. no current was flowing through the circuit) for 15 minutes and the voltage was recorded. The experiment was followed by recording the current at a constant voltage of 1 mV for another 15 minutes. In the third step, the
voltage was changed to 400 mV for the last 15 minutes and the current was recorded. The gas exhaust was recorded using the MS during the experiment. The first step showed a stable open circuit voltage of 0.94 V and the MS intensity of H₂ and CO with a m/e ratio of 2 and 29 (28 also represents CO but it has overlapping with other species) showed their maximum values. Since the current was zero and no oxygen ion was flowing from the cathode to the anode side, no oxidation reaction of the fuels occurred. Consequently the MS intensity of the oxidation reaction products including H₂O and CO₂ with a m/e ratio of 18 and 44 indicated their minimum values at OCV. After 15 minutes the condition switched to the constant voltage of 1 mV which is very close to the zero and results in highest current density and highest oxygen ion concentration. The current density was in a range of 520-560 mA/cm² at 1 mV. The MS intensity of the H₂ and CO was the lowest at this step which demonstrates the high consumption of the fuels due to the high concentration of the oxygen ions at high current density. Therefore, the MS intensity of the H₂O and CO₂ showed its maximum value at a constant voltage of 1 mV.

In the third step the voltage was switched from 1 mV to 400 mV which decreased the current density from 560 to 295 mA/cm². During the last 15 minutes the current density gradually decreased from 295 to 270 mA/cm². The MS intensity of the electrochemical oxidation reactants and products was in between the MS intensity at the first and second step of the experiment. The applied voltage on the cell was lower than the previous step resulting in lower current density and lower oxygen ion concentration which consumed less amount of H₂ and CO to produce H₂O and CO₂. Molar concentration of the reactants and products of the electrochemical reactions during the step changes were calculated from the MS intensities and current density to determine the contribution of each reaction.
to the overall electrochemical performance of the cell. The results of the molar
calculation will be presented in section 4.4.

Figure 4.11 Graph (a) MS intensity of the exhaust gas of the reactor (b) voltage and (c) current density profile at OCV, 1 and 400 mV of the cell with LSCF-Ni/YSZ anode at 800°C in He+ CO/H₂ during the step changes of voltage
4.3.3 Microstructure analysis of the LSCF-Ni fuel cell

Figure 4.12 shows the SEM image of the LSCF and Ni surface of the LSCF-Ni cell along with the EDX composition profiles. SEM image of the LSCF shows a homogen structure with small amount of agglomerated particles at the center of the picture. SEM micrograph of the Ni surface shows some bright micro-fiber on top of the Ni particles which can be the carbon fibers. Carbon peak in EDX profile could confirm the existence of small amount of carbon on the Ni surface. EDX of the LSCF surface displays the peaks of compositional elements for LSCF, namely La, Sr, Co and Fe.

Figure 4.13 shows the image of LSCF and Ni interface for the LSCF-Ni fuel cell along with the SEM micrograph of the interface and La, Ni and C mapping. From the mapping elemental analysis high density of La at the left and Ni at the right side can be seen which represents for the LSCF and Ni anode. Mapping of the carbon shows slightly higher density of the carbon on the right side which evidences higher deposition of the coke on Ni part than the LSCF. This can be attributed to the high oxygen ion conductivity of the LSCF which led to either direct oxidation of coke to produce CO$_2$ or formation of H$_2$O which further reacts with carbon to produce H$_2$ and CO [8].
Figure 4.12 Result of microstructure analysis (a) SEM micrograph of LSCF (b) SEM micrograph of Ni (c) EDX of LSCF and (d) EDX of Ni for the anode surface of the LSCF-Ni fuel cell
Figure 4.13 Result of microstructure analysis (a) interface image of LSCF and Ni (b) SEM micrograph of the interface (c) La mapping (d) Ni mapping and (e) carbon mapping of the interface for the anode surface of LSCF-Ni fuel cell
4.4 Calculation of molar concentration for the reactants and products

Molar concentrations of the reactants and products were calculated from the known amounts of reactants in the inlet stream, MS intensity of each species in outlet stream and total flow rate of the outlet. Concentration of the oxygen molecules was calculated based on the Faraday’s laws of electrolysis. Faraday’s laws state a relationship between the amounts of chemical change and electrical energy in an electrochemical reaction which is summarized in Eq.4.3 [39]

\[ n = \left( \frac{Q}{F} \right) \left( \frac{1}{z} \right) \]  

(4.3)

where \( n \) is the number of moles of the substance, \( Q \) is the total electric charge, \( F \) is Faraday constant equal to 96485 C/mol and \( z \) is the number of electrons transferred per 1 mole of substance.

During the cell operation at 800°C in addition to oxidation reactions of \( \text{H}_2 \) and \( \text{CO} \) (Eq.s 4.4 and 4.5), side reactions also occurred on the anode side, which resulted in the formation of methane according to Eq.s 4.6, 4.7 and 4.8 and formation of coke according to Eq.s 4.9 and 4.10 [8, 16-17, 38, 40-42].

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \]  

(4.4)

\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \]  

(4.5)

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

(4.6)

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

(4.7)

\[ 4\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \]  

(4.8)

\[ 2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C} \]  

(4.9)
\[ \text{CH}_4 \rightleftharpoons \text{C} + 2 \text{H}_2 \]  

(4.10)

CH₄ and coke also played a role as fuels (reactants) and underwent the electrochemical oxidation reactions to produce H₂O, CO₂, H₂ and CO according to Eq.s 4.11-4.15 [41-44].

\[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO} + 2 \text{H}_2 \]  

(4.11)

\[ \text{CH}_4 + \frac{3}{2} \text{O}_2 \rightleftharpoons \text{CO} + 2 \text{H}_2\text{O} \]  

(4.12)

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

(4.13)

\[ \text{C} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO} \]  

(4.14)

\[ \text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2 \]  

(4.15)

Molar concentrations of He, H₂, CO, CO₂, H₂O, CH₄ and C took into account for the calculation of each fuel contribution to the total current density. Table 4.2 shows the results of molar concentration calculation. The concentration of He remained constant in the inlet and outlet streams. The concentration of H₂ and CO as reactants decreased in the outlet stream due to their consumption in oxidation reactions.

At OCV the oxygen concentration was zero and no oxidation reaction occurred on the anode surface of the cells. The reactants, H₂ and CO, showed their maximum values and the products, H₂O and CO₂, showed their minimum values at OCV. At 1 mV the oxygen concentration was the highest and the highest amounts of reactants were consumed via the electrochemical oxidation reactions which resulted in lowest concentration of reactants and highest concentration of products. At 400 mV the concentrations of the oxygen, reactants and products were in between those at OCV and 1 mV.
Table 4.3 shows the molar concentrations of the oxygen molecules and net consumption and production of the reactants and products from the electrochemical oxidation of H₂, CO, CH₄ and coke. The reported values for H₂O and CO₂ at OCV in Table 4.2 resulted from the previous reactions which were not related to the step changes experiment (OCV to 1 mV to 400 mV) since there is no oxidation reaction at OCV condition. Based on this fact the net consumption and production of the reactants and products in Table 4.3 were obtained by subtracting the concentrations at OCV from the concentrations at 1 mV and 400 mV.

Figure 4.14 shows the percentage of oxygen consumption by each of the fuels, namely H₂, CO, CH₄ and coke for the Ni and LSCF-Ni cells at 1 mV. This figure shows higher oxygen consumption by H₂ than CO for Ni anode cell suggesting that the oxidation of H₂ was the dominant oxidation reaction for a cell with Ni anode. This is in agreement with the result of voltage-current measurement which indicated almost similar performance of the cell in H₂/CO and in H₂ suggesting that the oxidation of H₂ was the dominant reaction in a mixture of H₂ and CO for Ni anode. The oxygen consumption by H₂ and CO is about the same for a cell with LSCF-Ni anode suggesting that the oxidation reaction of H₂ and CO proceeded in parallel for LSCF-Ni anode. By adding the LSCF to the Ni the rate of oxidation reaction of CO was increased and it could compete with the H₂; therefore, both oxidation reactions took place in parallel. This can be confirmed by the result of voltage-current measurement which showed that the performance of the cell with LSCF-Ni anode in H₂/CO was in between the performance in H₂ and in CO separately. Figure 4.14 also indicates higher oxidation of coke over the LSCF-Ni than the Ni anode surface which resulted in lower amount of coke deposition on the anode.
surface. This can be attributed to the high oxygen ion conductivity of the LSCF that provides higher amount of oxygen ion for direct oxidation of carbon [8]. Figure 4.15 shows the percentage of oxygen consumption by each of the fuels for the Ni and LSCF-Ni cells at 400 mV which demonstrates similar trend and carries the same concept as Figure 4.14. It can be seen form Figure 4.14 and Figure 4.15 that the contribution ratio of H₂ to CO for total current density generation is about 3 to 1 for Ni anode and it is 5 to 4 for LSCF-Ni anode which is in agreement with previous results.
### Table 4.2 Molar concentrations of reactants and products at OCV, 1 mV and 400 mV

<table>
<thead>
<tr>
<th>Gaseous species</th>
<th>Ni Inlet (µmol/s)</th>
<th>Ni Outlet (µmol/s)</th>
<th>LSCF-Ni Inlet (µmol/s)</th>
<th>LSCF-Ni Outlet (µmol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C&lt;sub&gt;OCV&lt;/sub&gt;</td>
<td>C&lt;sub&gt;1 mV&lt;/sub&gt;</td>
<td>C&lt;sub&gt;400 mV&lt;/sub&gt;</td>
<td>C&lt;sub&gt;OCV&lt;/sub&gt;</td>
</tr>
<tr>
<td>He</td>
<td>33.88</td>
<td>33.88</td>
<td>33.88</td>
<td>33.88</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>16.94</td>
<td>6.94</td>
<td>6.61</td>
<td>16.94</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0</td>
<td>9.33</td>
<td>9.91</td>
<td>9.69</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
<td>1.13</td>
<td>1.61</td>
<td>1.38</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0</td>
<td>0.33</td>
<td>0.28</td>
<td>0.32</td>
</tr>
</tbody>
</table>

### Table 4.3 Molar concentrations of the oxygen molecules and net consumption and production of the reactants and products during the step changes experiment for Ni and LSCF-Ni cells

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔC&lt;sub&gt;1 mV-OCV&lt;/sub&gt; (µmol/s)</th>
<th>ΔC&lt;sub&gt;400 mV-OCV&lt;/sub&gt; (µmol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.47</td>
<td>-0.35</td>
</tr>
<tr>
<td>CO</td>
<td>-0.17</td>
<td>-0.32</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.67</td>
<td>0.48</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.47</td>
<td>0.72</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>-0.05</td>
<td>-0.03</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.24</td>
<td>1.44</td>
</tr>
</tbody>
</table>
Figure 4.14 Percentage of oxygen consumption by H₂, CO, CH₄ and coke for the Ni and LSCF-Ni cells at 1 mV

Figure 4.15 Percentage of oxygen consumption by H₂, CO, CH₄ and coke for the Ni and LSCF-Ni cells at 400 mV
CHAPTER V
CONCLUSION

This study was focused on two objectives, LSCF synthesis and determining the contribution of each fuel to total current density generation. XRD crystallography of the LSCF powder synthesized by the rapid combustion method demonstrated a pure perovskite phase of the LSCF with rhombohedral structure. SEM micrographs indicated the porous structure of the synthesized LSCF and resistivity measurement showed high electrical conductivity similar to that of standard calcined LSCF powders. This result demonstrated that the rapid combustion for LSCF synthesis is a promising method for substitution of the standard calcination methods.

To achieve the second objective, a cell with Ni anode was tested in H₂, CO and H₂/CO. The electrochemical measurements and effluent gas analysis revealed that Ni anode displayed a similar behavior in H₂/CO to that in H₂, which indicates the dominance of H₂ oxidation during the oxidation of CO/H₂ mixture. The contribution of H₂ oxidation to total current density generation was about three times higher than that of CO oxidation for the cell with Ni anode. Synthesized LSCF was added to the Ni to fabricate a cell with LSCF-Ni anode in order to observe possible changes in contribution of H₂ and CO to current density generation. The electrochemical measurements and effluent gas analysis revealed that the contribution of CO oxidation and H₂ oxidation was about 5 to 4. This
suggests that the LSCF changed the pathway of anode reactions to be more favorable toward CO oxidation. The study also revealed higher oxidation of coke over the LSCF-Ni than the Ni anode surface which resulted in lower amount of coke deposition on the anode surface. This can be attributed to the high oxygen ion conductivity of the LSCF that provides higher amount of oxygen ions for direct oxidation of carbon.
REFERENCES


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This section provides the supplementary results of Ni and LSCF-Ni fuel cells including impedance, MS, current density, XRD, SEM and EDX data.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy is a useful technique for electrical characterization of multi-processes electrochemical systems such as fuel cells. In this type of complicated dynamic systems, steady state polarization curves are not useful since they can only identify the reaction mechanisms of simple systems with a single rate-determining step. Impedance spectroscopy applies a small signal perturbation to reveal the relaxation time and relaxation amplitude (dynamic behavior) of each physical and chemical process contributing to the internal resistance of the cell over a wide range of frequencies.

When a current flow passes through an electrochemical cell, the cell voltage deviates from its reversible value (Eq.2.4) and this deviation is called as overpotential. Polarization resistance of a cell can be identified with known values of current and overpotential. In complicated systems such as fuel cells, there is a non-linear relationship
between voltage and current which cannot be identified by direct current (DC) measurement; therefore alternating current (AC) measurement must be applied to determine the polarization resistance of the cell. The response to the AC input is shown by Nyquist plot which generally consists of two semicircles at high (left side) and low (right side) frequency ranges. Ohmic resistance of the cell is determined from the length between the imaginary axis and the intersection of the high frequency semicircle. Total resistance of the cell is the length between the imaginary axis and the intersection of the low frequency semicircle and the polarization resistance is the difference between the total and ohmic resistance [45][46].

Figure A.1 Impedance spectra of the cell with Ni/YSZ anode measured at OCV and 800°C in (▲) He+H₂, 100 sccm, 50 vol% H₂; (■) He+CO, 100 sccm, 50 vol% CO; and (●) He+H₂ /CO, 100 sccm, 25/25 vol% H₂/CO
Figure A.2 Impedance spectra of the cell with LSCF-Ni/YSZ anode measured at OCV at 800°C in (▲) He+H₂, 100 sccm, 50 vol% H₂; (■) He+CO, 100 sccm, 50 vol% CO; and (●) He+H₂/CO, 100 sccm, 25/25 vol% H₂/CO
Figure A.3 Graph (a) MS intensity of the exhaust gas of the reactor and (b) current density profile at 400 mV of the cell with Ni/YSZ anode at 800°C while switching the inlet gases from He+H₂ to He and from He to He+CO
Figure A.4 Graph (a) MS intensity of the exhaust gas of the reactor and (b) current density profile at 400 mV of the cell with Ni/YSZ anode operating at 800°C while switching the inlet gases from He+CO to He+CO/H₂.
Figure A.5 Graph (a) MS intensity of the exhaust gas of the reactor and (b) current density profile at 400 mV of the cell with LSCF-Ni/YSZ anode operating at 800°C while switching the inlet gases from He+CO to He+ CO/H₂
Figure A.6 XRD patterns of the surface deposited carbon (coke) of Ni and LSCF-Ni anodes
Figure A.7 Result of microstructure analysis (a) SEM micrograph (b) carbon mapping and (c) EDX of the cross section of LSCF-Ni fuel cell
APPENDIX B

CHARACTERIZATION OF SYNTHESIZED LSCF

IR spectroscopy of synthesized LSCFs

Figure B.1 FT-IR DRIFTS background spectra of calcined and combusted LSCF diluted with KBR
Figure B.2 FT-IR DRIFTS background spectra of combusted LSCF diluted with KBR
FT-IR DRIFTS background spectra of LSCF in Ar

Figure B.3 FT-IR DRIFTS background spectra of calcined $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}$ diluted with varying ratio of $\text{CaF}_2$ (with citric acid, without EG) in Ar
Figure B.4 FT-IR DRIFTS background spectra of calcined La$_{0.8}$Sr$_{0.2}$Co$_{0.4}$Fe$_{0.6}$ diluted with varying ratio of CaF$_2$ (with citric acid, without EG) in Ar
Figure B.5 FT-IR DRIFTS background spectra of calcined $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}$ diluted with varying ratio of $\text{CaF}_2$ (with citric acid, without EG) in Ar

XRF characterization of synthesized LSCFs

<table>
<thead>
<tr>
<th>Table B.1 XRF results of LSCFs</th>
<th>La</th>
<th>Sr</th>
<th>Co</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}<em>{0.8}\text{Sr}</em>{0.2}\text{Co}<em>{0.4}\text{Fe}</em>{0.6}$</td>
<td>calcined</td>
<td>55.96</td>
<td>13.25</td>
<td>12.75</td>
</tr>
<tr>
<td>+CA+EG</td>
<td>burnt</td>
<td>56.41</td>
<td>11.87</td>
<td>13.12</td>
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<tr>
<td>$\text{La}<em>{0.6}\text{Sr}</em>{0.4}\text{Co}<em>{0.2}\text{Fe}</em>{0.8}$</td>
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<td>44.07</td>
<td>25.05</td>
<td>6.3</td>
</tr>
<tr>
<td>+CA+EG</td>
<td>burnt</td>
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<td>23.72</td>
<td>6.44</td>
</tr>
<tr>
<td>$\text{La}<em>{0.8}\text{Sr}</em>{0.2}\text{Co}<em>{0.4}\text{Fe}</em>{0.6}$ +CA</td>
<td>calcined</td>
<td>55.96</td>
<td>13.67</td>
<td>12.7</td>
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<td>burnt</td>
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<td>57.85</td>
<td>10.47</td>
<td>12.99</td>
</tr>
<tr>
<td>$\text{La}<em>{0.6}\text{Sr}</em>{0.4}\text{Co}<em>{0.2}\text{Fe}</em>{0.8}$ +CA</td>
<td>calcined</td>
<td>44.98</td>
<td>23.12</td>
<td>7.07</td>
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<td>burnt</td>
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<td>43.62</td>
<td>24.79</td>
<td>6.31</td>
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<td>$\text{La}<em>{0.8}\text{Sr}</em>{0.2}\text{Co}<em>{0.4}\text{Fe}</em>{0.6}$</td>
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<td>2.04</td>
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<tr>
<td>burnt</td>
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<td>10</td>
<td>13.36</td>
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<tr>
<td>$\text{La}<em>{0.6}\text{Sr}</em>{0.4}\text{Co}<em>{0.2}\text{Fe}</em>{0.8}$</td>
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<td>20.93</td>
<td>6.87</td>
</tr>
<tr>
<td>burnt</td>
<td></td>
<td>50.08</td>
<td>14.34</td>
<td>7.39</td>
</tr>
<tr>
<td>$\text{La}<em>{0.6}\text{Sr}</em>{0.4}\text{Co}<em>{0.2}\text{Fe}</em>{0.8}$ Nextec</td>
<td>-</td>
<td>44.21</td>
<td>24.23</td>
<td>6.68</td>
</tr>
</tbody>
</table>
XRD crystallography of synthesized LSCFs

Figure B.6 XRD patterns of the synthesized LSCF8246 and LSCF6428