Effect of Manufacturing Technique on Electrochemical Response of a Sulfur Tolerant Planar Solid Oxide Fuel Cell Anode

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the Russ College of Engineering and Technology of Ohio University

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Master of Science

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This thesis titled
Effect of Manufacturing Technique on Electrochemical Response of a Sulfur Tolerant
Planar Solid Oxide Fuel Cell Anode

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the Department of Chemical and Biomolecular Engineering
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ABSTRACT


Director of Thesis: David J. Bayless

Strontium doped lanthanum vanadate (La$_{0.7}$Sr$_{0.3}$VO$_3$, LSV) is a sulfur tolerant anode material capable of selectively oxidizing H$_2$S over H$_2$ and chemical, electrical and thermal properties of this material have been studied to date. This research attempted to determine the best thickness of LSV/YSZ bi layer anodes operating on coal syngas containing 300 ppm H$_2$S at 800 °C and 900 °C, based on electrochemical response. Screen printing technology was used as the low cost method to manufacture anodes. The best anode thickness at 800 °C was 65 μm while 80 μm was the best thickness at 900 °C. The results suggested that the anode performances were governed by catalytic activity of LSV, resistance to electron transfer and the length of gas diffusion paths which was a function of anode thickness. The cell microstructures exhibited an undisturbed porous structure at the electrode electrolyte interface after 48 hour test runs.

Approved: _____________________________________________________________

David J. Bayless

Loehr Professor of Mechanical Engineering
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1.1 Background of the research

Coal is an abundant resource in most continents of the world and in the year 2004 in the USA alone, coal based power accounted for approximately 50% of the country’s total electric power generation [1]. Recognition of clean coal technology in the United States national energy policy and large price differentials versus other fuels have ignited coal research.

If coal is to thrive as an energy source, gaseous emissions which accompany coal fired power generation must be reduced. “FutureGen” is a proposed 275 MW research power plant in the United States which will aim at generating electricity and hydrogen from coal, while capturing and sequestering green house gases like carbon dioxide emitted during the process [2]. Operation of a high temperature solid oxide fuel cell in conjunction with a coal gasifier for generation of power becomes promising with the development of new fuel cell technologies [3].

The efficiency of a solid oxide fuel cell nears 50%. However in a hybrid system with gas turbines it may be possible to reach 70% and with waste heat recovery, efficiencies could even reach 80-85% [4].

Two types of solid oxide fuel cells have been commercialized to date, namely planar SOFCs and tubular SOFCs. Due to advantages such as ability to operate at higher current densities and lower cost of manufacturing, this research focuses on high temperature planar solid oxide fuel cells.
In a SOFC the anode is fed with a fuel gas while the cathode is supplied with an oxidant, which is often an air supply, and these two streams react electrochemically on active sites in the anode and cathode respectively. Coal syngas can be used as fuel and comprises gaseous constituents such as carbon monoxide, carbon dioxide, hydrogen, nitrogen, water vapor, and hydrogen sulfide. A conventional solid oxide fuel cell with a Ni/YSZ anode operating on such a gas mixture is faced with the problem of sulfur poisoning by H$_2$S. Sulfur poisoning is identified as the formation of NiS on the anode, which obstructs the catalytic activity of nickel and diminishes electrical conductivity. At the same time NiS lowers melting point of the anode, leading to melting of the anode during SOFC operation [5].

Various composite materials which tolerate presence of hydrogen sulfide in the fuel are being studied [5]. Recently one such composite, namely strontium-doped lanthanum vanadate (LSV) has been found to exhibit promising sulfur tolerant characteristics and has been studied extensively at Georgia Institute of Technology [5]. The study has revealed that strontium-doped lanthanum vanadate is among the most sulfur-tolerant materials reported so far and its selective oxidation of hydrogen sulfide increases catalytic activity with ascending H$_2$S concentrations [5].

Strontium doped lanthanum vanadate (La$_{0.7}$Sr$_{0.3}$VO$_3$) cannot be considered as a composite with significant electronic conductivity when compared with other possible anode materials. Despite low electronic conductivity, Cheng et al. have shown that LSV has noteworthy characteristics as a hydrogen sulfide scrubbing unit, thus supporting solid oxide fuel cell operation in a sour gas environment [6].
Various properties of strontium doped lanthanum vanadate have been studied by Cheng et al. employing different configurations of the La$_{1-x}$Sr$_x$VO$_3$ perovskite [7]. However, the anode thickness of a particular cell configuration has not been optimized for a sulfur tolerant high temperature solid oxide fuel cell to date highlighting the need for the current research, as anode thickness directly influences gas diffusion to the electrochemical reaction sites. In addition electrode thickness influences resistance to electron transfer. Further screen printing as a manufacturing method of electrodes is a low cost technique compared to other methods of depositing an electrode layer on an electrolyte substrate as suggested by Singhal and Kendall [8].

1.2 Objectives

This research will use screen printing technology as the technique for manufacturing bi-layer anodes containing LSV catalyst and YSZ electrolyte component. Once the cells are made, the next focus of this work is to quantify selective oxidation characteristics of LSV/YSZ anodes of six different thicknesses via experimentation. Further, determining anode thicknesses at 800°C and 900 °C that provide the best electrochemical responses is the final area of focus of this research.

Voltage current characteristic curves are observed at 800 °C and 900 °C and cell impedance spectra are recorded at desired intervals as the active sites along the thickness directly influence resistance to charge transfer. Thicknesses of anodes are measured using the infinite focus microscope (profilometer) and correlated to the electrical performance of the SOFCs. Potentiostatic tests are used to understand cell degradation via cell power
densities. Post analysis of anode microstructure should reveal changes in microstructure of the cell and identify deposition of carbon or any other material during the process.

The Figure 1.1 illustrates the basic arrangement of the intended experimental procedure. The Ohio Coal Research Center fuel cell group members use common button cell test stands and have similarities in experimental set up. In addition the proposed research supports Matthew E. Cooper’s PhD research work [9].

![Figure 1.1: Basic experimental procedure [9]](image)

This project is expected to provide data that might help to deploy a fuel cell system comprising a LSV scrubbing unit in series with a conventional Ni/YSZ solid oxide fuel cell.
CHAPTER 2
LITERATURE REVIEW

2.1 Operation of a solid oxide fuel cell

A solid oxide fuel cell comprises four main components, namely the anode, electrolyte, cathode and interconnects. Fuel gas is supplied to the anode while the cathode is supplied with the oxidant, which is often atmospheric air. The electrolyte is an ionic conductor that conducts oxygen ions from cathode to anode [9]. It does not conduct electrons in contrast to the porous electrodes and is a dense structure. Figure 2.1 shows the arrangement of a solid oxide fuel cell unit.

![Image showing the arrangement of a solid oxide fuel cell unit](image)

Figure 2.1: An exploded view of a solid oxide fuel cell (reproduced from [10])

The anode and cathode reactions of a solid oxide fuel cell fueled by hydrogen or carbon monoxide are as given in Equations 2.1-2.3. The Nernst potentials of overall reactions 2.1 and 2.2 are 1.03 V and 0.94 V at 900 °C and an operating pressure of one atmospheric, respectively.
Anode with H₂: \[ \text{H}_2 + \text{O}^{-2} \rightarrow \text{H}_2\text{O} + 2\text{e}^{-} \quad (2.1) \]
Anode with CO: \[ \text{CO} + \text{O}^{-2} \rightarrow \text{CO}_2 + 2\text{e}^{-} \quad (2.2) \]
Cathode: \[ \text{O}_2 + 4\text{e}^{-} \rightarrow 2\text{O}^{-2} \quad (2.3) \]

2.2 Operating a solid oxide fuel cell on coal syngas

A typical oxygen blown coal syngas composition will be comprised of carbon dioxide, hydrogen, nitrogen, carbon monoxide, moisture and small amounts of hydrogen sulfide. Use of such a gaseous mixture to operate a solid oxide fuel cell has produced significant research interest [11].

A conventional solid oxide fuel cell with a Ni/YSZ anode, YSZ electrolyte and LSM cathode is at risk of sulfur poisoning in a H₂S environment. Hydrogen sulfide reacts with the Ni/YSZ anode forming NiS which subsequently halts desired electrochemical reactions [12], leading to research on sulfur tolerant anode materials. At the Georgia Institute of Technology, an anode material of strontium doped lanthanum vanadate (LSV) has been identified to possess promising behavior in the presence of hydrogen sulfide [5].

2.3 Strontium doped Lanthanum Vanadate (LSV)

LSV is a ceramic which belongs to the family of Perovskites (ABO₃ configuration). Its properties can be altered by varying the amount of strontium and lanthanum [5]. Aguilar et al. have found that La₀.₇Sr₀.₃VO₃ has the ability to selectively oxidize H₂S [13]; however it does not have the electron conducting properties such as the conventional Ni/YSZ anode [5]. Figure 2.2 below shows the ABO₃ perovskite structure as explained by Aguilar [5].
Aguilar et al. identified the following possible reactions at a LSV anode of a solid oxide fuel cell operating on hydrogen sulfide and air [5].

\[
\begin{align*}
H_2S + O^{2-} & \rightarrow \frac{1}{2} S_2 + H_2O + 2e^- \quad (2.4) \\
H_2S + 3O^{2-} & \rightarrow SO_2 + H_2O + 6e^- \quad (2.5)
\end{align*}
\]

According to Aguilar, SO₂ formation (Equation 2.5) is more prominent with an increase in fuel utilization. However, Hui and Petric revealed that LSV is unstable in an oxidizing environment due to formation of an irreversible Sr₃V₂O₈ phase which diminishes electrical conductivity [14].
2.4 La\textsubscript{0.7}Sr\textsubscript{0.3}VO\textsubscript{3} as a scrubbing unit

Cheng et al. studied operation of a SOFC fueled by a 5% H\textsubscript{2}S and 95% CH\textsubscript{4} gas mixture. Table 2.1 lists the compositions in the cell exhaust stream during their testing [6]. The SOFC was comprised of a La\textsubscript{0.7}Sr\textsubscript{0.3}VO\textsubscript{3} anode, a YSZ electrolyte, and the cathode was a LSM/YSZ composite. The voltage-current-power characteristic curves of the above cell are given in Figure 2.3.

**Table 2.1: Exhaust compositions of 5% H\textsubscript{2}S and 95% CH\textsubscript{4} operating at 950 \textdegree C [6]**

<table>
<thead>
<tr>
<th>Species</th>
<th>E=OCV \textsubscript{i=0}</th>
<th>E=-0.7V \textsubscript{i=160mA/cm\textsuperscript{2}}</th>
<th>E=-0.5V \textsubscript{i=400mA/cm\textsuperscript{2}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}</td>
<td>32.86%</td>
<td>20.79%</td>
<td>12.09%</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>63.74%</td>
<td>71.27%</td>
<td>76.87%</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>1.52%</td>
<td>5.67%</td>
<td>6.87%</td>
</tr>
<tr>
<td>H\textsubscript{2}S</td>
<td>1.37%</td>
<td>1.12%</td>
<td>2.72%</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>0.14%</td>
<td>0.41%</td>
<td>0.79%</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>0.07%</td>
<td>0.22%</td>
<td>0.31%</td>
</tr>
<tr>
<td>CS\textsubscript{2}</td>
<td>0.30%</td>
<td>0.52%</td>
<td>0.36%</td>
</tr>
</tbody>
</table>

The values in Table 2.1 indicate that as the current density is improved, the amount of H\textsubscript{2}S in the exhaust is increased. Figure 2.3 shows high power densities corresponding to high current densities. This implies that a SOFC using a LSV anode cannot maximize selective oxidation and power output simultaneously.

As a result, and given the previously mentioned low electron conducting properties of LSV, it is suggested by Cooper [9] that La\textsubscript{0.7}Sr\textsubscript{0.3}VO\textsubscript{3} can be used as a H\textsubscript{2}S scrubbing unit which protects a downstream conventional SOFC which uses a Ni/YSZ anode. Recently Cheng et al. have studied various properties of La\textsubscript{0.7}Sr\textsubscript{0.3}VO\textsubscript{3}
However there have not been experimental investigations with direct focus on effect of thickness on the LSV anode’s performance.

2.5 Electrode manufacturing techniques

Various methods are used in the industry to manufacture planar solid oxide fuel cell anodes depending on the type of fuel cell namely electrolyte supported cells and anode or cathode supported cells. Sun and Stimming describes screen printing and tape casting as the widely used methods for producing anodes of electrolyte supported cells while atmospheric plasma spraying, vacuum plasma spraying laser reactive deposition are newer technologies used in other types of anodes [15].

2.5.1 Screen printing

Rotureau et al. investigated screen printing technology to develop planar solid oxide fuel cells and this method was used to manufacture both two chamber and single chamber PSOFCs [16]. A thickness of 20 μm has been achieved with a single print [16], however screen printing is followed by high temperature sintering which may be a time consuming step in the process [15].

2.5.2 Tape casting

Yoon et al. used tape casting to manufacture anode support structures where the anode composites are mixed with binder, dispersant and pore formers. Anode supports manufactured in this manner measured approximately 1 mm in thickness while the electrolyte and the cathode are applied with screen printing technique [17].
2.5.3 Slurry painting and brush painting

Jiang and Virkar manufactured a bi layer Ni/YSZ anode with slurry coating. The inter layer measured 20 μm while the total anode thickness was 1.1 mm. However screen printing has been used to apply the LSC cathode layer [18]. Cheng et al. brush painted slurries of anode and cathode composites on either side of the YSZ electrolyte [6]. However it is believed that with manual brush painting it may not be able to have a proper control of the thickness of the layer applied.

2.5.4 Combustion chemical vapor deposition (CCVD)

Liu and Liu used combustion chemical vapor deposition to manufacture a 200 μm thick bi layer anode of an anode supported PSOFC. In this manufacturing process CCVD was used to produce the composite powder for the anode by initially dissolving metal constituents in an organic solvent followed by combusting in an oxygen methane environment [19].

2.6 Importance of anode thickness

In a SOFC both the anode and the cathode are essentially porous structures while the electrolyte is a dense structure. Hayre et al. illustrated the involvement of gas pores in the concept of triple phase boundary (TPB) as shown in Figure 2.4 [20].
Figure 2.3: Vi–Pi curves of the SOFC operating with pure H₂ and H₂S/CH₄ mixture (reproduced from [6])

When the fuel gas enters the anode, it is oxidized by giving up electrons which can take place only in specified regions identified as triple phase boundaries, or the contact zones for electrode, electrolyte and gas pores [20]. Ivers and Virkar have identified the reaction mechanism in the SOFC anode [8]. First, fuel gas molecules are adsorbed on to the surface of the electrode catalyst, which is followed by the surface reaction. During the surface reaction the adsorbed molecules diffuse through pores to the triple phase boundary, where the fuel gives up electrons to form water and carbon dioxide in the case of a fuel comprising hydrogen and carbon monoxide [8]. As such it is evident that the length of pores which is the path of gas diffusion to the electrode electrolyte interface is a function of the electrode thickness. Further electrode thickness influences
diffusion time and on certain occasions may be adversely affected by tortuous paths due to the longer route to active sites. In bi layer anodes comprising different compositions of catalyst and electrolyte components, it is possible to enhance triple phase boundaries over the anode thickness. However, the anode thickness should be an optimum value since a very high thickness will promote concentration overpotential as shown in Figure 2.5 and Figure 2.6 [21] for anode supported structures. Similarly, a very thin anode is deprived of enhanced reaction sites and may even result in leakage currents highlighting the necessity to optimize anode thickness of a bi layer anode in an electrolyte supported PSOFC.

In a fuel cell, voltage losses also known as polarization losses occur in the form of activation polarization, ohmic polarization, and concentration polarization. Activation losses are caused due to reaction kinetics, while ohmic polarization occurs due to resistance to charge transfer [8]. Concentration polarization can be attributed to mass
transport losses [8]. Ivers and Virkar have explained that charge transfer in electrodes is a function of "electronic resistivities" [8]. In electrolyte supported fuel cells the major contributor to ohmic polarization is the electrolyte due to high ionic resistivity compared to those of the electronic resistivities of the anode and the cathode as explained by Tiffee and Virkar [8].

Figure 2.5: Vi-power curves at different thicknesses of an anode supported SOFC (reproduced from [21])
Figure 2.6: Concentration overpotential at different anode thicknesses for an anode supported SOFC (reproduced from [21])
CHAPTER 3

EXPERIMENTAL SET UP

3.1 An overview of the experiments

This research attempts to provide information that may be useful in employing a system combining a conventional Ni/YSZ SOFC which is fueled by coal syngas. In this way the system is hypothesized to be able to utilize H₂S-containing feeds. In the research, anode thicknesses are correlated to performance of the SOFCs. LSV/YSZ bi layer anodes are screen printed on half cathode button cells, sintered in a furnace and operated in a button cell test stand where fuel and air are supplied via a gas delivery system. Microstructure of the anode is analyzed using SEM, EDXS and XRD while a Solartron analytical system is used to analyze the SOFCs’ electrical performance.

3.2 Hionic cells

As the experiments are performed on button cells operating at 800 °C and 900 °C, Hionic button cells from Nextech Materials are used in all test runs as they have been designed for high temperature SOFC applications. These electrolyte supported button cells are 28 mm in diameter, which is the electrolyte while its two layer LSM/GDC cathode is 12.5 mm in diameter. Such a button cell has an electrolyte thickness of 150 μm and cathode has an approximate thickness of 100 μm. The anodes with thicknesses of 50, 65, 80, 95, 110 and 125 μm are screen printed at the Ohio Coal Research Center laboratory.
3.3 Anode ink preparation

La$_{0.7}$Sr$_{0.3}$VO$_3$ powder (Praxair, 99.9%), 8 mole % YSZ (Tosoh) and organic binder (Heraeus) are thoroughly mixed in preparing LSV/YSZ ink (Table 3.1) which is to be screen printed as the anode layer. The binder is expected to form bonds supporting the structure during sintering and is responsible for some of the voids created in addition to the inherent pores in the LSV/YSZ anode material structure.

**Table 3.1: Bi layer anode compositions**

<table>
<thead>
<tr>
<th>Weight % of Constituents</th>
<th>Anode Layer</th>
<th>Inner Layer</th>
<th>Top Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSV (20m$^2$/g)</td>
<td>LSV (30m$^2$/g)</td>
<td>YSZ (13.1m$^2$/g)</td>
<td>YSZ (135m$^2$/g)</td>
</tr>
<tr>
<td>25%</td>
<td>20%</td>
<td>25%</td>
<td>50%</td>
</tr>
<tr>
<td>50%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4 Screen printing

The LSV/YSZ ink is screen printed on the Hionic Cell electrolyte, using the AMI Presco Screen Printer 465, which has the ability to control thickness of the print layer by adjusting blade height, angle and speed [22]. It may be suggested that screen printing could also be used to vary packing of material layers by varying pressure applied. The inter layer is maintained at a thickness of 30 μm while the top layer will provide the balance of the desired thickness.
3.5 Sintering

The screen printed test samples are sintered in a ST-1600-888 AG High Temperature Furnace under a reducing atmosphere (2% H₂, 98% Ar) at a temperature of 925 °C, during which volatile matter will be released from the anode layer creating much needed active sites for the desired electrochemical reaction. It is important to maintain the sintering temperature below 1350 °C to avoid build up of an insulating lanthanum zirconate layer on the cathode side [23]. The inter layers are screen printed and sintered before applying the top layer.
3.6 Anode thickness measurements with the Infinite Focus Microscope (Profilometer)

Images of screen printed LSV/YSZ bi layer anodes are taken via the infinite focus microscope at a suitable magnification which provides clear images. Profiles are taken at different locations along the anode periphery to ensure the consistency of the anode thickness over the anode area. The infinite focus microscope is capable of measuring thicknesses in the nanometer range and is located in the test facility available at the Institute of Corrosion and Multiphase Technology, Ohio University.

3.7 Material analysis

The microstructures of button cell anodes are studied using material analysis techniques before and after experimental runs on the button cells. The data collected is used to identify existing material phases before tests, post-test new material phase build up, changes to anode microstructure and delamination at the electrode electrolyte interface. Further, deposition of foreign material on the anode and pore distribution is studied to understand cell characteristics. The techniques used are Scanning Electron Microscopy (SEM) for anode microstructure; Energy Dispersive X-ray Spectroscopy (EDXS) for observing existence of elements especially sulfur and carbon while X-Ray Diffraction (XRD) is used for identification of material phases. This work will be performed in the Clippinger and Corrosion Center Laboratories of Ohio University.

3.8 Button cell test stands and gas delivery

The button cells will be tested in the Test Stands that are being installed in the (OCRC) Ohio Coal Research Center laboratory. The anode and cathode gases will be
regulated via mass flow controllers (Alicat Scientific), while temperature controllers (Watlow) will ensure proper furnace operation. The mass flow controllers have maximum flow rates of 20, 10, 20, 5, 20 and 3500 sccm for H$_2$, CO$_2$, CO, CO/H$_2$S blend, N$_2$ and air respectively. It is believed that these flows are sufficient to deliver the fuel to the SOFC and avoid starving of cells. The anode will be fired in a reducing atmosphere (H$_2$) for a time period of two hours prior to test runs [24]. The gaseous composition which fuels the cells has constituent concentrations similar to that of gasified Pittsburgh no.8 coal (Table 3.2).

**Table 3.2: Composition of oxygen blown Pittsburgh no. 8 coal [25]**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>12</td>
</tr>
<tr>
<td>H$_2$</td>
<td>29.1</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.1</td>
</tr>
<tr>
<td>CO</td>
<td>28.6</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>27.1</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>300 ppm</td>
</tr>
</tbody>
</table>
They are mixed and fed to the anode of the button cell. The cathode is supplied with a volume of air which contains approximately five times the stoichiometric requirement of O₂. A bubbler provides water injection to the fuel stream to achieve the desired composition and also in the event of preventing coking in the cells. The experiments focus on a post steady state continuous operation time period of 48 hours [24].

3.9 Analyzing electrical performance on Solartron

The voltage- current curve of a cell is a key indicator of cell characteristics at any time of operation. A combination of a platinum paste coat and a Ni mesh are used to collect current while, current leads will be of silver (Ag). Once a button cell is loaded in
to the test furnace temperature is ramped up to 800 °C from room temperature at a ramp rate of 2 °C/min in a reducing atmosphere. Initially N₂ is fed at 20 ml/min to the anode and gradually decrease the N₂ rate and increase H₂ to 20 ml/min over an 8 hour time period. The open circuit voltage (OCV) is observed using the Solartron analytical 1480 Multistat System [26] for the next hour and it will indicate electrochemical oxidation of H₂ and in the following hour the temperature is ramped up to 900 °C. Total test time for observing electrochemical response is 48 hours and following the initial ramp up fuel composition is changed from pure H₂ to coal syngas after the first 16 hours. This composition is changed to coal syngas with H₂S after another 16 hours and will remain unchanged until the end of test run. Voltage current scans based on potentiostatic tests are taken during operation on each gas composition to identify maximum current densities reached by different anode thicknesses. At suitable intervals the cells are operated potentiostatically at 0.7 V study cell power densities and change in performance due to variation in gas composition. The Solartron impedance analyzer is used to measure cell impedance especially the charge transfer resistance influenced by electrochemical oxidation of different gaseous species. Figure 3.7 below illustrates a complex plane impedance spectrum for an electrochemical process which identifies impedances due to ohmic resistance (Rₛ), charge transfer resistance (Rₐ) and mass transport resistance (Rₐ) [8, 27]. During experimental runs in order to obtain, impedance spectrum, frequency (ω) of the electrical system is varied from 300000 Hz to 0.1Hz at a biased voltage of 0.7V and an AC amplitude of 70mV. Total cell impedance is measured due to the difficulty in
placing the reference electrode to measure impedance of individual layers as explained by Mogensen and Hendriksen [8].

![Complex plane impedance spectrum](image)

Fig 3.3: Complex plane impedance spectrum (adapted from [27])

3.10 Safety, materials handling and regulations

All equipment and instruments will be used in line with the Ohio Coal Research Center Standard Operating Practice guidelines. Any new and existing chemicals/gases will be stored, handled and disposed according to the standards specified and in consultation with the Environmental Health and Safety division of Ohio University.
CHAPTER 4
TEST PLAN AND MATIRX

The objective of this work is to study how different anode thicknesses affect the electrochemical response of an electrolyte supported solid oxide fuel cell at two different temperatures, in the presence of H₂S-containing coal syngas. This experimental study is focused on the use of LSV to be used as a sulfur tolerant anode in a SOFC. An upstream LSV/YSZ/LSM/GDC/LSM cell is used as an electrochemical reactor to selectively oxidize H₂S in coal syngas, which in turn prevents formation of undesirable NiS in a downstream conventional Ni/YSZ cell.

In the experiment, the fuel gas used has approximately the same composition as gasified Pittsburgh no. 8 coal in Table 3.2. A button cell with an electrode diameter of 12.5mm and electrolyte diameter of 28mm is used as the test cell. Effects of variation of anode thickness is studied by VI- characteristic curves obtained during operating the cells on H₂, coal syngas and coal syngas with H₂S. Cell power densities at different stages of operation are found through potentiostatic tests. Electrochemical impedance spectroscopy (EIS) is used to observe variation in cell impedance as a function of anode thickness. Different thicknesses imply variation in material content which in turn alters resistance to charge transfer and length of gas diffusion paths to the triple phase boundaries.

Anode thickness is measured using the infinite focus microscope which uses a software to generate the height distribution (profile) of the anode. XRD, SEM and EDXS are performed to analyze pre and post test material phases and foreign material deposition.
4.1 Button cells with bi layer anode

A two layer cathode is used where lanthanum strontium manganite/ gadolinia doped ceria (LSM 20/GDC10) occupies the inter layer while LSM20 acts as the current collector layer. These are the standard compositions of button cells manufactured at Nextech Materials and in general LSM/GDC composites have better performances over LSM cathodes due to mixed ionic electronic properties [28]. LSM/GDC ink screen printed on to a yttria stabilized zirconia electrolyte enhances catalytic activity sites of the phase boundaries [28]. GDC though electronically insulating, possesses noteworthy catalytic characteristics. Further, the 70% to 30% volume ratio used in LSM/GDC composites manufactured at NexTech is the mix which provides best conductivity and catalytic activity (J. Foreman, pers. comm.). Different compositions of LSV/YSZ are employed as the inter layer and top layer in the anode which promote catalytic activity towards electrochemical oxidation of H₂S while improving triple phase boundaries and matching thermal properties of each layer.

4.2 Fuel gas

Known compositions of CO₂, H₂, N₂, CO, H₂O and H₂S which are similar to those produced in gasification of Pittsburgh no. 8 coal, are fed to the anode side of the solid oxide fuel cell. A C-H-O ternary diagram such as in Figure 4.1 helps identify regions of carbon deposition corresponding to gases in the fuel [29]. On the C-H-O phase diagram mole fractions of atomic carbon, hydrogen and oxygen resulting from constituent gases are plotted and the intersection of these plots as shown in Figure 4.1 is considered to be the operating point. Lines drawn through corner H of the triangle represent the thresholds...
beyond which carbon deposition occurs when operating at 700 °C and 900 °C respectively. Coking is be prevented by altering H₂O content by increasing the water temperature in the bubbler, thus preventing clogging of pores in electrodes that provide sites for electrochemical reactions. According to the ternary diagram the chosen coal syngas composition is in a non coking region. However, if there is a need to alter the moisture composition from 27.1%, the temperature of the bubbler can be varied via heat applied through heat tapes attached to the bubbler.

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**Figure 4.1:** C-H-O phase diagram at 1073 K (adapted from [30])
4.3 Anode thickness and electrochemical activity

SOFC anodes are porous structures and existence of voids allow for substantial contact between fuel, electrodes and electrolyte. As the experiments are focused on optimizing anode thickness, electrochemical responses are observed at two different temperatures. This enables to see the influence of temperature on catalytic activity of the electrode. Resistance of materials decreases with increasing temperature, as such anode current densities are expected to be lower at 800 °C. According to Nerst Equation the open circuit voltages recorded at 900 °C should be lower than at 800 °C.

Maximum current density recorded under each gas composition is crucial in optimizing the anode thickness based on electrical performance and VI characteristic curves provide the necessary information. EIS data presents charge transfer resistance that maybe helpful in clarifying results associated with VI scans. Resistance to electron transfer mounts with increasing anode thickness while lower thicknesses offer low resistance. However higher anode thicknesses enhances triple phase boundaries. When the anode thickness is very low it may not be able to provide the hydrogen oxidation required to satisfy the electron demand from cathode due to lack of active sites.

4.4 Material tests

Microstructure of test samples is examined before and after experiments, with a combination of techniques such as SEM, EDXS and XRD. Each technique will provide semi-quantitative/qualitative information and a combination of all methods will provide the best information.
XRD is performed in finding out the existing material phases after sintering anode furnace and is compared with material supplier data. This technique is used as the initial material analysis after test runs to identify defects in crystal structure, change in material phases and existence of foreign material. This is followed by gold sputtering of samples to generate scanning electron microscope images. These images are taken at appropriate magnifications is used to study post experiment microstructure an electrode top surface as well as anode electrolyte interface. This is helpful in identifying areas on the electrode which underwent delamination or any significant material agglomeration due to operating conditions and confirm compatibility of the anode layer with the electrolyte in a coal syn gas environment. In general, a SOFC electrode’s interlayer will possess a “greater porosity than other areas while maintaining a coarser micro structure” [8].

Energy dispersive x-ray analysis is performed on points selected with the aid of SEM images and is be used to investigate existence of possible elements. This method is combined with XRD patterns to confirm prevailing material phases. At high temperatures there is a possibility of H₂S and SO₂ reacting to form elemental sulfur and H₂O in the anode [5] and EDXS is useful in identifying such sulfur depositions. As organic binder is mixed with LSV ink, there is a possibility of carbon containing compounds to remain in the anode clogging pores and is investigated using the above technique.

4.5 Test matrix

Anodes of six different thicknesses (Table 4.1) with a replicate from each thickness are operated on syngas at two different temperatures and involve a total of 24
test runs, with each being 66 hours approximately including furnace ramp up and ramp down. Further each thickness will have a ± 5 micron tolerance to account for practical difficulties in screen printing.

**Table 4.1: Test matrix with variable parameters**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Anode thickness (2 replicates from each)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 μm</td>
<td>65 μm</td>
</tr>
<tr>
<td>800 °C</td>
<td></td>
</tr>
<tr>
<td>900 °C</td>
<td></td>
</tr>
</tbody>
</table>

Electrochemical tests (Table 4.2) will include potentiostatic tests for power density analysis, voltage current (Vi) scans and electrochemical impedance spectroscopy (EIS). Post experiment material analysis is performed using SEM, EDX and XRD.

**Table 4.2: Electrochemical Tests**

<table>
<thead>
<tr>
<th>Gas Composition</th>
<th>Electrochemical Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>Vi Scans</td>
</tr>
<tr>
<td>Coal Syngas</td>
<td></td>
</tr>
<tr>
<td>Coal Syngas with H2S</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 5
MANUFACTURING ELECTRODES WITH SCREEN PRINTING

This chapter describes the process used to manufacture anodes for solid oxide fuel cell applications. In addition, this chapter discusses functions available in the screen printer that was used on manufacturing anodes of different thicknesses, challenges encountered and useful information for future users.

5.1 Thick film screen printer

Presco Thick Film Screen Printer model 465 manufactured by Affiliated Manufacturers Inc. owned by the Ohio Coal Research Center was used for in-house production of bi-layer electrodes. Figure 3.1 in the Experimental Set Up section shows the screen printer that was used for manufacturing anodes.

5.2 Controlling the electrode thickness

There are four functions available in the screen printer to control the thickness of the electrode being printed namely; squeegee pressure, snap off distance, squeegee speed and angle of the blade. Before attempting screen printing on single sided cells it is best that the user keeps three of these functions at a fixed setting and understand the effect of varying the fourth variable function. As such the user must practice printing on plain substrates, sinter the ink in a furnace at desired conditions of the material and finally measure the thickness of the layer printed using the profilometer or any other appropriate thickness measuring device.
5.2.1 Squeegee pressure

Squeegee pressure can be varied by rotating the squeegee pressure micrometer clockwise or counter clockwise (Fig 5.1). It is important to note that the applied pressure affects packing of layers on top of each other thus varying the void percentage of the electrode. Sometimes it may not be possible to get a print with the first stroke of the squeegee blade. This is directly attributable to the ink being printed. As such it is prudent for the users to acquire an understanding of the ink’s relative viscosity.

![Squeegee head](image)

**Figure 5.1: Squeegee head**

5.2.2 Snap off distance

Snap off distance is the height between the bottom surface of the screen and the top surface of the carriage as shown in Figure 5.2. It may be varied using the Z-
adjustment knob located at the rear of the screen printer and the distance can be measured with a feeler gauge. In the event of printing with a low viscosity ink that easily penetrates the mesh area of the screen, the above gap should be controlled to avoid splashing.

Figure 5.2: Squeegee head lifted pneumatically to apply ink on the screen

5.2.3 Squeegee speed

The squeegee speed, the speed at which the blade travels, can be adjusted to vary both the forward and backward motion speed. The speed controlling “extend” and “retract” knobs are shown in Figure 5.3. If the ink being printed is relatively viscous, the blade may have to be used at a low speed to give sufficient time for the ink to permeate
the mesh. Further, screen printing a viscous ink at a high speed may result in an uneven print or a thin layer.

Figure 5.3: Squeegee speed extend and retract

5.2.4 Angle of attack (θ)

As shown in Figure 5.4, the angle of attack is found between the face of the blade and horizontal in the forward stroke. It can be adjusted by rotating the angle of attack adjustment knob, which is shown (Fig 5.2). Even a minor change in angle creates a significant impact on the printing and the ink layer applied is also being influenced by the blade material. Whenever the angle of attack is adjusted printing should be tested with a dry run to identify the degree of pressure being applied by the blade to avoid damage to the screen which can easily get scratched.
5.2.5 Useful information for screen printing

In addition to the screen printer functions that can be used to achieve the desired thickness there are other factors that influence printing. First, the print is dependent on the friction factor or roughness of the surface on which the print is being applied. At the same time the tension of the screen also affects the printing and the same screen should be used for printing a batch of replicates to maintain consistency in the packing factor of the electrode layer. When screen printing a bi-layer electrode, the inner layer should be applied and sintered before printing the top layer to control thickness. Figure 5.5 shows a bi-layer anode screen printed on to a substrate manufactured by Nextech and Figure 5.6 shows the corresponding profile of the anode thickness near the periphery of the anode. The top portion of Figure 5.6 is the magnified image of the profile area as taken from the infinite focus microscope. The profile of the anode proves the motion of the squeegee blade makes it difficult to achieve the desired thickness at the edges of the electrode. However it is observed that the thickness reaches the intended value less than a micron into the electrode thus making the unevenness at the boundary negligible.
Figure 5.5: A screen printed LSV/YSZ anode
Figure 5.6: Image and profile of the printed anode near the anode periphery
CHAPTER 6
RESULTS AND DISCUSSION - ELECTRICAL TESTS

The purpose of this chapter is to review the electrochemical results from testing of selective oxidation characteristics of LSV anodes with different thicknesses by using button cells comprising LSV/YSZ bi-layer anodes. Voltage-current (Vi) characteristic curves were generated at 800°C and 900 °C and cell impedances spectra recorded at desired intervals. Potentiostatic tests were used to understand cell degradation measured by cell power density response.

6.1: Electrochemical responses at 800 °C

Initially the LSV/YSZ button cells were operated at 800 °C to investigate the maximum current densities that could be achieved by cells with different anode thicknesses. Electrochemical reactions occur in active sites dispersed in the anode which comprised of catalyst and electrolyte in both inner layer and outer layer. The degree of electrochemical activity at 800 °C which was at the lower temperature limit of high temperature solid oxide fuel cells, needed to be identified and related to thickness. Figures 6.1, 6.2 and 6.3 show the voltage variation as function of current density for different anode thicknesses operating on H2, simulated coal syngas and simulated coal syngas with H2S respectively as given in Table 3.2. Performances of replicates at each thickness were within 5 % and were considered satisfactory for comparison. At 800 °C the SOFCs indicated maximum open circuit voltages of 0.88, 0.92 and 0.91 V while operating on the three different gas compositions. The theoretical maximum open cell voltage for H2 was calculated to be 0.98 V (Appendix A) at 800 °C and 1 atm. It is quite
possible that the lower than expected OCVs were mainly due to fuel leakage through mica seals used in the experiment. The highest current density at 0.3 V was recorded using the 65 μm anode for all different gas compositions while the lowest current density was found consistently using the 50 μm anode. The rest of the anode thicknesses showed an intermediary performance with no clear pattern for anode behavior based on thicknesses.

Figures 6.4, 6.5, and 6.6 show the impedance spectra (Nyquist plots) obtained for different anode thicknesses operating on H₂, coal syngas, coal syngas with H₂S respectively. These curves were a combination of several points observed while the frequency was swept from 300000 Hz to 0.1 Hz. The length of the vector joining the origin and any point of the Nyquist plot is the magnitude of the impedance at the selected frequency. In the Nyquist plots the closest point to the origin at which any curve meets the x axis represents the area specific resistance (ASR) of the cell which is a measure of the internal resistance. The right-most point at which the curve touches the x axis represents the total of internal resistance and charge transfer resistance. The charge transfer resistance which is equivalent to the diameter of Nyquist plots was used as a measure of the speed of the electrochemical reaction as well as the length of the triple phase boundary in which the reaction take place. This resistance was lowest for the 65 μm anode which agrees with the highest current densities recorded in the Vi characteristic curves, while 50 μm anode too indicates similar pattern with the highest charge transfer resistance. Further the charge transfer resistances for rest of the thicknesses are analogous to the trend observed in maximum current density variation. The cathode thickness of the
cells used was 100 μm and it may be possible that the 50 μm anode thickness lacked active sites to aid the full potential of the cathode for oxygen reduction. While the 65 μm anode was the best performer, it may be possible that the other anodes were influenced by higher thicknesses which offer a greater electronic resistivity and mass transfer losses.

Figure 6.7 shows voltage and power density variation with current density for the best thickness 65 μm at 800 °C for the previously described gas compositions. The maximum power densities calculated from Vi scans were approximately 6 mW/cm² which verifies the low electronic conductivity and catalytic oxidation towards H₂ compared to conventional Ni/YSZ anodes. Figure 6.8 shows the impedance spectra obtained for the same cell. It is noticeable that charger transfer resistance has been lowest during operation on coal syngas and highest during operation on coal syngas with H₂S. This trend is visible in the power density curves obtained through potentionstatic tests (0.7V) at different time intervals and plotted on the same graph as shown in Figure 6.9. There is an increase in power density during coal syngas feed and a drop during introduction of H₂S. It is a possibility that during operation on coal syngas, the Ni mesh employed as the current collection mesh catalyzed water gas shift reaction and during H₂S injection the Ni mesh has been poisoned. The power curve for syngas with H₂S recovers back to the pure H₂ power density level indicating that carbon monoxide is no longer converted to H₂. This behavior suggests that LSV is not a catalyst for water gas shift reaction which converts CO to H₂ and there is no electrochemical oxidation of CO in the presence of an LSV anode.
Figure 6.1: Vi characteristic curves for different anode thicknesses operating on H₂ at 800 °C
Figure 6.2: Vi characteristic curves for different anode thicknesses operating on coal syngas at 800 °C
Figure 6.3: Vi characteristic curves for different anode thicknesses operating on coal syngas with H₂S at 800 °C
Figure 6.4: Impedance spectra for different anode thicknesses operating on H$_2$ at 800 °C
Figure 6.5: Impedance spectra for different anode thicknesses operating on coal syngas at 800 °C
Figure 6.6: Impedance spectra for different anode thicknesses operating on coal syngas with H₂S at 800 °C
Figure 6.7: Voltage and power density vs. current for the optimum thickness (65 μm) at 800 °C
Figure 6.8: Impedance spectra for optimum anode thickness (65 μm) at 800 °C