DEVELOPMENT OF SOLID OXIDE FUEL CELLS UTILIZING ALTERNATIVE FUELS

A Dissertation in

Energy and Mineral Engineering

by

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Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

May 2012
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This dissertation is a summary of four solid oxide fuel cell (SOFC) research projects which addressed a number of SOFC technologies to use alternative fuels (other than H₂, natural gas, and CO) and culminated in the development of a solid oxide fuel cell (SOFC) anode design that is shown to generate electrical power by the oxidation of solid hydrocarbon fuel (coal) without external reformation.

Chapters 1 and 2, demonstrate the current state and limitations of SOFC operation on alternative hydrocarbon fuel sources. A common limitation in traditional SOFC systems is the inability to directly oxidize heavy liquid hydrocarbons due to carbon deposition coking or solid hydrocarbons due to fuel transport limitations. External reformation (Chapter 2) is often used to overcome these limitations but at the cost system efficiency due to the chemical energy consumed in the reformation process.

The contribution to the science and technology of electrochemistry presented here is the development of a liquid metal anode solid oxide fuel cell (LMA-SOFC) system capable of generating electrical power from the direct electrochemical oxidation of coal; as well as the development of a test system and protocol for the performance evaluation of new liquid metal or liquid alloy anode materials. Chapters 3 and 4 present the development and operation of the LMA-SOFC system and test procedure. The LMA-SOFC system developed is shown to generate electrical power from hydrogen and coal, and is evaluated with electrical impedance spectroscopy and equivalent circuit modeling to further understand the chemical and electrochemical reaction mechanism. The system also identifies the durability of anode materials in high current operation.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... vii

LIST OF TABLES ................................................................................................................ ix

ACKNOWLEDGEMENTS ................................................................................................. x

Introduction ....................................................................................................................... 1

- Solid Oxide Fuel Cell Fundamentals ........................................................................... 1
- Liquid Metal Anode Solid Oxide Fuel Cell Fundamentals ........................................... 3
- Equivalent Circuit Modeling of Impedance Spectra ..................................................... 4
- Introduction References ............................................................................................... 6

Chapter 1: Degredation in Solid Oxide Fuel Cells Operating with Alternative Fuels ........................................................................................................................... 7

- Preface ......................................................................................................................... 7
- Abstract ....................................................................................................................... 8
- Introduction ............................................................................................................... 8
- Experimental System and Procedure .......................................................................... 10
- Results and Discussion .............................................................................................. 12
  - Heavy Hydrocarbon Fueled SOFC: Jet Fuels & Crude Oil ........................................ 12
  - Waste Vegetable Oil Fueled SOFC ........................................................................... 13
  - Ethanol-Water Blend Fueled SOFC ........................................................................ 14
  - Bio-diesel Fueled SOFC ........................................................................................... 15
- Conclusion .................................................................................................................. 20
- Chapter 1 References ................................................................................................. 21

Chapter 2: Solid Oxide Fuel Cell Fueled by Diesel Reformate and Anaerobic Digester Gas ...................................................................................................................... 23

- Preface ......................................................................................................................... 23
- Abstract ....................................................................................................................... 24
- Introduction ............................................................................................................... 24
- Experimental System and Procedure ........................................................................ 25
  - Fuel Chemistry, Cleaning and Reforming ................................................................. 25
  - Solid Oxide Fuel Cell Materials and Preparation ...................................................... 26
  - Test System and Equipment .................................................................................... 27
  - Electrochemical Testing ........................................................................................... 28
- Results and Discussion .............................................................................................. 29
  - Anaerobic Digester Gas ............................................................................................ 31
  - Commercial Diesel Steam Reformate ....................................................................... 33
- Conclusion .................................................................................................................. 34
Summary .............................................................................................................................. 86
Conclusions ......................................................................................................................... 87
Suggestions for Future Research ......................................................................................... 88
LIST OF FIGURES

Figure 0-1 Schematic of solid oxide fuel cell with reaction mechanism steps overlaid for the electrochemical oxidation of H₂ and CO. ........................................ 1

Figure 0-2 Representation of reaction mechanism in hydrogen and carbon fueled LMA-SOFC. ........................................................................................................ 4

Figure 0-3 Figure 0-3. LMA-SOFC impedance spectra generated by inert Ar fed anode, equivalent circuit model and results................................................................. 5

Figure 1-1 Potential and power density vs. current density at three different flow rates for Cu-ceria fuel cell at 700 °C. ................................................................. 16

Figure 1-2 Potential and power density vs. current density at three different flow rates for Ce-Rh fuel cell at 700 °C................................................................. 17

Figure 1-3 Potential and current density vs. time for Cu-ceria fuel cell at 700 °C...... 18

Figure 1-4 Potential and current density vs. time for Ce-Rh fuel cell at 700 °C........ 19

Figure 2-1 Schematic of the integrated commercial diesel steam reformer and solid oxide fuel cell system........................................................................................................ 28

Figure 2-2 Performance curve (cell potential vs. current density) of SOFC fueled by hydrogen, anaerobic digester gas and diesel reformate at 900 °C.................. 30

Figure 2-3 Electric power generation curve (power density vs. current density) of SOFC fueled by hydrogen, anaerobic digester gas and diesel reformate. .............. 31

Figure 2-4 Impedance spectra generated by hydrogen fueled and anaerobic digester gas fueled SOFC at 900 °C with air fed anode. ............................................ 32

Figure 3-1 Representation of reaction mechanism in hydrogen and carbon fueled LMA-SOFC. ........................................................................................................ 39

Figure 3-2 Membrane electrode assembly of LMA-SOFC; during operation “anode chamber” is filled with humidified nitrogen, humidified nitrogen-hydrogen blend, or coal under humidified nitrogen. .................................................. 44

Figure 3-3 Backscattered electron image of the Sn-Pb alloy used as anode material in the LMA-SOFC ....................................................................................... 46

Figure 3-4 Linear potential sweep data for Sn-Pb LMA-SOFC at 900 °C under an inert nitrogen anode environment................................................................. 49
Figure 3-5. Linear potential sweep data for Sn-Pb LMA-SOFC at 900 °C, with a hydrogen-fueled anode.

Figure 3-6 Coal-fueled Sn-Pb LMA-SOFC at 900 °C; OCP increases from a single 0.05 g coal injection to the anode surface while under nitrogen.

Figure 3-7 Coal-fueled Sn-Pb LMA-SOFC at 900 °C; power generation resulting from the application of an external electronic load following coal injections.

Figure 4-1 Schematic of crucible LMA-SOFC.

Figure 4-2 Equivalent circuit models used in fitting LMA-SOFC.

Figure 4-3 Impedance spectra generated by cathode symmetric cell.

Figure 4-4 Impedance spectra generated by liquid tin anode SOFC.

Figure 4-5 Impedance spectra and equivalent circuit modeling results for inert argon anode LMA-SOFC.

Figure 4-6 Impedance spectra generated by LMA-SOFC under argon, dry-coal and coal-water slurry anode feeds.

Figure 4-7 Cell potential vs. current density generated by fresh LMA-SOFC.

Figure 4-8 Cell potential sweeps and current response degradation generated by fresh LMA-SOFC.

Figure 4-9 Impedance spectra generated by LMA-SOFC before and after degradation.
LIST OF TABLES

Table 1-1 Open circuit potential (OCP) in volts of SOFC operated with different fuel blends as a function of temperature................................................................. 14

Table 2-1: Comparison of SOFC performance parameters for different types of alternative fuels........................................................................................................... 33

Table 3-1. Standard thermodynamic properties of liquid metal and fuel oxidation redox couples........................................................................................................ 42

Table 4-1 Equivalent circuit modeling resistance parameters used in fitting LMA-SOFC impedance spectra.............................................................................. 75
ACKNOWLEDGEMENTS

Chapter 1 Acknowledgments
This research was supported by the Department of Energy (Contract # DENT0004396). The authors thank Dr. Victor Balashov (EMS Energy Institute, Penn State University) for assistance with impedance spectroscopy measurements.

Chapter 2 Acknowledgments
Funding provided for the work by the U.S. Department of Energy through the National Energy and Technology Laboratory (Project # DE-FC26-08NT0004396) is fully acknowledged.

Chapter 3 Acknowledgments
We acknowledge Earth and Mineral Sciences Energy Institute, Coal Utilization Laboratory, Materials Research Institute and Materials Characterization Laboratory at Penn State University, and the US Department of Energy, National Energy Technology Laboratory (NETL) for financial support of this work. Special thanks are to R. Gorte, J. Vohs, and R. Kungas (University of Pennsylvania) for useful discussions in the early stage of this project.

Chapter 4 Acknowledgments
We acknowledge Earth and Mineral Sciences Energy Institute, Coal Utilization Laboratory, Materials Research Institute and Materials Characterization Laboratory at Penn State University, and the US Department of Energy, National Energy Technology Laboratory (NETL) for financial support of this work. A contribution to the equivalent circuit modeling of oxygen diffusion coupled through the liquid metal anode with a coupled with kinetic reaction parameters was made by Sanchit Khurana.

Personal Acknowledgments
I would like to personally thank and acknowledge my academic advisor Dr. Serguei Lvov; as well as my committee members: Dr. Harold Schobert, Dr. Semih Eser and Dr. Michael Janik for their support and encouragement in my undergraduate and graduate studies. I would like to extend my appreciation to Bruce and Sharon Miller, Ronnie Wasco, Ronald Wincek and Bradley Maben for their role in facilitating and promoting my undergraduate fuel research. I would also like to thank Justin Beck for assistance in preparing the document and intellectual criticism. Finally, I would like to express my appreciation and personal debt to the United States Department of Energy for their financial, intellectual and material support of these and so many other scientific endeavors.
Introduction

Solid Oxide Fuel Cell Fundamentals

Solid oxide fuel cells (SOFC) have been studied in-depth and shown to co-generate electrical power and heat with efficiencies that outperform even the most advanced combustion technologies. Several detailed literature reviews of SOFC technology and development have been composed and are widely available [1,2].

![Solid Oxide Membrane: O²⁻ Ion Conductor](image)

**Figure 0-1.** Schematic of solid oxide fuel cell with reaction mechanism steps overlaid for the electrochemical oxidation of H₂ and CO.

The fundamental phenomenon exploited in SOFCs is the conductivity of negatively charged oxygen ions through certain dense ceramic materials, most commonly
yttria-stabilized zirconia (YSZ). A SOFC schematic that demonstrates the basic principles of the reaction mechanism is provided in Figure 0-1. The reaction mechanism taking place in the electrochemical oxidation of hydrogen fuel in a SOFC is as follows: 

O$_2$ is reduced from air at the cathode to form O$^{2-}$ ions; these ions are then conducted through the dense YSZ membrane to an anode catalyst; finally, the O$^{2-}$ ions electrochemically oxidize a fuel (H$_2$ or CO) fuel to produce H$_2$O and release two electrons that travel through an external circuit where they dissipate their power before returning to the cathode to participate in the oxygen reduction.

The materials found in common SOFC designs include the previously mentioned YSZ, 6-8% Y$_2$O$_3$ in ZrO$_2$, to function as the ionically conductive membrane. The useful range for O$^{2-}$ conductivity in YSZ is 650 to 1200 °C, and typical operation is between 800 to 1000 °C. The SOFC cathode, where O$_2$ is reduced to O$^{2-}$, is commonly a porous lanthanum strontium manganite (LSM) La$_{1-x}$Sr$_x$MnO$_3$ (where x is commonly between 0.1-0.2). The SOFC anode, where fuel is reduced, is often a porous Ni-YSZ cermet (a ceramic metal mixture).

Due to the conduction of oxygen ions from the air, rather than ions originating in the fuel, a few hydrocarbon fuels can be oxidized in SOFCs. Hydrogen is often used as a base-line fuel for performance characterization. However, natural gas, methane and carbon monoxide are commonly used and are considered more practical for large-scale SOFC implementation. Heavier hydrocarbon fuels have been oxidized in SOFCs with limited success; this work will expand upon the knowledge of SOFCs ability to oxidize solid hydrocarbons by employing equivalent circuit modeling to the impedance spectra generated by liquid metal anode solid oxide fuel cells under a variety of fuel conditions.
**Liquid Metal Anode Solid Oxide Fuel Cell Fundamentals**

A new approach to SOFC anode design is a liquid metal anode solid oxide fuel cell (LMA-SOFC). In LMA-SOFCs, the traditional anode materials are replaced with a pool of molten metal. This liquid metal is oxidized electrochemically in a manner similar to a metal-air battery; however, the novel approach is to regenerate the liquid metal from its oxide by a direct chemical reaction between the metal oxide and fuel.

The reaction mechanism proceeding within a LMA-SOFC fueled by hydrogen is depicted in Figure 0-2. The mechanism begins with the reduction of \( \text{O}_2(\text{g}) \) to \( \text{O}^{2-} \) ions at the LSM cathode, and these ions are conducted through the YSZ membrane where they electrochemically oxidize the liquid metal (Sn for this example) to its metal oxide (SnO\(_2\)), freeing electrons to dissipate their energy in an external load before returning to the cathode to complete the circuit. Finally, the liquid metal is regenerated by the chemical reduction of metal oxide by the fuel source (\( \frac{1}{2}\text{SnO}_2 + \text{H}_2 \rightarrow \text{Sn} + \text{H}_2\text{O} \)). A similar mechanism is predicted to occur in the oxidation of carbon-containing fuels.

\[
\begin{align*}
\text{H}_2(\text{g}) + \frac{1}{2}\text{SnO}_2(\text{s}) & \rightarrow \frac{1}{2}\text{Sn(l)} + \text{H}_2\text{O(}g) \\
\text{C(s)} + \text{SnO}_2(\text{s}) & \rightarrow \text{Sn(l)} + \text{CO}_2(\text{g})
\end{align*}
\]
Figure 0-2. Representation of reaction mechanism in hydrogen and carbon-fueled LMA-SOFC.

Equivalent Circuit Modeling of Impedance Spectra

A powerful tool in understanding the behavior of electrochemical cells is impedance spectroscopy. By alternating the electrical potential applied to a system at a variety of frequencies and monitoring the current response an impedance spectrum can be obtained. The data generated by impedance spectroscopy is the impedance magnitude (ratio of applied potential to current response), phase angle (delay between peak in applied potential and peak in current response) and frequency of alternating applied potential. This technique allows for a unique insight into the source of impedance contributions by separating impedances by relaxation time.

The impedance spectra generated by SOFCs are similar to that of some common electronic circuits. Equivalent circuit modeling of SOFC allows for the quantification of individual impedance contributions to the overall cell impedance. This technique separates the impedance contributions based on their relaxation time. In practice one can isolate the ionic, kinetic and mass transport impedance contributions of an electrochemical cell, and by applying symmetric cell analysis (Chapter 4) the contributions from the anode, cathode and membrane can be further isolated. Figure 0-3 demonstrates the accuracy with which equivalent circuit modeling can parallel impedance
data generated by LMA-SOFCs. Detailed literature reviews of impedance spectroscopy and equivalent circuit modeling are available [3,4].

Figure 0-3. LMA-SOFC impedance spectra generated by inert Ar fed anode, equivalent circuit model and results.
Introduction References


Chapter 1

Degradation in Solid Oxide Fuel Cells Operating with Alternative Fuels


Preface to Chapter 1

This chapter will emphasize the foundational work in applying an electrochemical impedance spectroscopy analysis to the equilibrium conditions of SOFCs fueled by alternative fuels. The work reported in this chapter contains a review of the research carried out at Penn State University by Z. Zhou, C. Gallo, M. Pague, R. Kumar, S. Thakur, L. Rudnick, H. Schobert and S. Lvov on the direct oxidation of heavy liquid hydrocarbons in solid oxide fuel cells focusing on the performance and degradation in the SOFC.

The experimental contributions made by the primary author (M. LaBarbera) include the performance and degradation characterization of solid oxide fuel cells fueled by ethanol-water blends including preliminary investigation of the impedance spectra generated by the ethanol fueled SOFC.
Abstract

Solid Oxide Fuel Cells (SOFCs) have been shown to generate power with a wide variety of hydrocarbon based fuels. The operation of SOFCs with alternative fuels is hindered by carbon deposition and sulfur poisoning. Here we analyze the performance and degradation of SOFCs with different types of anode, including Ni-YSZ, Cu-ceria, and Rh-ceria based anodes. The tested fuels include Pennsylvania crude oil, JP-7 and JP-8 Plus jet fuels, waste vegetable oil, ethanol, and biodiesel. The performance of the cell with each fuel was characterized with cell voltage vs. current density curves, degradation tests, and electrochemical impedance spectroscopy measurements.

Introduction

Fuel cells have been widely investigated due to the potential of highly efficient and clean power production resulting from electrochemical processes as opposed to traditional heat engines. Solid oxide fuel cells (SOFC) are based on solid electrolyte membranes, typically yttria-stabilized zirconia (YSZ), which has high ionic conductivity at temperatures above 500 °C. The high operating temperatures of SOFC facilitate the kinetics of electrode reactions and provide more flexibility with catalytic materials compared to PEM fuel cells. It has been shown that many common hydrocarbon fuels can be directly oxidized in SOFC (1-5). In our laboratory, previous studies were performed on direct utilization of jet fuels, crude oil (6), and waste vegetable oil (7). While the perspective of direct utilization of hydrocarbons is very attractive economically, there is a number of challenges to solve, which include carbon deposition on the anode (8-10),
decreased cell performance with alternative electrode components (10, 11), and poisoning of the catalysts by various impurities (12).

Alcohols (primarily methanol and ethanol) currently receive special attention as renewable fuels that can be produced from biomass. Ethanol’s high energy density, clean burning, and ease of handling would make it an appropriate fuel for transportation and storage. The use of ethanol as SOFC fuel has been reported in several studies. In SOFC with Ni-YSZ anodes, carbon deposition was observed with pure ethanol, but was successfully suppressed by mixing ethanol with water (13-15). It is inferred that operating temperature for ethanol-fueled SOFC may be an important tuning factor, since, on one hand, it controls the kinetics of the in-situ reforming reaction (more efficient conversion at higher temperature) (13), but, on the other hand, affects carbon deposition (less deposit at lower temperature) (16). Relatively stable performance with ethanol was obtained with alternative perovskite anodes at 800 °C (17).

With each particular fuel type, the picture of SOFC performance degradation can be quite complex and needs detailed investigation for finding an efficient remedy. There are a number of electrochemical techniques employed to study the performance and degradation of SOFC with different fuels. Electrochemical impedance spectroscopy (EIS) is regarded as a powerful technique for cell life and degradation studies (18, 19). In the generated Nyquist plots (Zimag vs. Zreal) obtained by EIS, the arcs generated in low frequency region (0.1-100 Hz) represent diffusion and gas conversion, the arcs measured in high frequency region (100-10K Hz) are associated with the electrode polarization resistance in the anode and cathode processes, and the intercept at high frequency is determined by the total ohmic resistance of the electrolyte and interfaces between the
electrodes and electrolyte. The electrode polarization resistance indicates the anode and cathode polarization loss and reaction kinetics. Thus, the possible degradation in SOFC electrodes during long term fuel cell test can be monitored by impedance measurements with respect to the change in the electrode kinetics and diffusion resistance as a function of time (20, 21). Performance degradation due to carbon deposition and sulfur poisoning, and its reversibility has been previously studied by EIS for a variety of hydrocarbon based fuels (22, 23).

In this chapter, we report some selected results on SOFC operation with a few types of heavy hydrocarbon fuels, including Pennsylvania crude oil, jet fuel, and waste vegetable oil, ethanol-water blend, and biodiesel.

**Experimental System and Procedure**

As each fuel provides its own factors toward SOFC degradation, several different experimental methods and SOFC anode compositions were used in this study. The SOFCs used in the testing of Pennsylvania crude oil and JP-7 and JP-8 Plus jet fuels were prepared using the method developed by researchers at the University of Pennsylvania (2, 24, 25). These fuel cells consisted of a dense YSZ (Tosoh TZ-8Y), 60 μm thick, membrane, Cu-ceria anode, and LSM cathode. For biodiesel tests, both Cu-ceria and Rh-ceria anodes were used. The design of the test apparatus was reported elsewhere (6, 7). The system allowed for the injection of liquid or gaseous fuels. These fuels were diluted with N2 gas and vaporized while being injected toward the Cu-ceria anode. Humidified air was provided to the cathode. The crude oil used in these experiments was obtained
from Well 64, Warren, PA, USA, with Glade formation; no further processing was done to this fuel prior to use. The JP-7 and JP-8 Plus jet fuels were obtained from the US Air Force, Dayton, OH, USA. The waste vegetable oil was taken directly from the fryers of a local fast food restaurant; then passed through an alumina filter. Gas chromatography mass spectrometry (GC/MS) data (7) showed that the vegetable oil mainly consisted of triglyceride, perhaps with some traces of oxidation products. The sulfur contents in the tested fuels were as follows: 910 ppm in the crude oil, 10 ppm in JP-7, 475 ppm in JP-8 Plus, and 2.33 ppm in the waste vegetable oil. All tests were carried out at 700°C (973 K).

The SOFCs used in the testing of ethanol were button cells obtained from Fuel Cell Materials Inc. The cells were 20 mm in diameter and consisted of the 120 μm thick YSZ electrolyte layer, Ni-YSZ anode, and LSM cathode. The electrode diameter was 12.5 mm, which provided the electrode area of 1.23 cm² on both anode and cathode sides. As current collectors, gold wire coil was attached onto the anode with gold ink, and a platinum mesh with platinum wire was attached onto the cathode with platinum ink, and the cell was sintered at 850°C for 1 hour. For the test, the cell was mounted on an alumina tube using CAP-552 SOFC sealing paste (Fuel Cell Materials inc.), anode positioned towards inside the tube, and the whole assembly was step-cured at 93°C and 260°C for 2 hours at each temperature. The mounted cell was installed in a tube furnace, using a holder with separate fuel and air lines. The design of the experimental system was similar to the one described in (6). This system provided the ability to switch between gaseous or liquid fuels. The cell was conditioned by running H₂/N₂ gas mixture and pure H₂ as fuels during the first 24 hours of operation. Open circuit voltage (OCV) measurements and
performance tests were performed repeatedly to check the cell functionality. Next, ethanol-water blend was injected to the anode compartment using a syringe pump at a rate of 76.3 μl/min. The fuel mixture was diluted with nitrogen and is assumed to have fully vaporized prior to reaching the cell. Humidified air was supplied to the cathode side of the cell at a flow rate of 128 ml/min through a coiled capillary. All tests were performed at ambient pressure and three temperatures: 650, 750, and 850°C.

The electrochemical measurements in this study were carried out using a Gamry Instruments Reference 600 Potentiostat /Galvanostat/ZRA. In particular, electrochemical impedance spectroscopy (EIS) measurements were carried out to observe the ohmic resistance of the cell as well as variations in polarization resistances with temperature and time. The EIS measurements were carried in a wide frequency range.

Results and Discussion

Heavy Hydrocarbon Fueled SOFC: Jet Fuels & Crude Oil

Similar performance had been observed in the operation of Cu-ceria SOFCs operating with Pennsylvania crude oil, JP-7, and JP-8 jet fuels. Open circuit voltages (OCV) of about 0.8 V were obtained with varying concentrations of the crude oil and jet fuels tested. This depressed OCV is similar to that observed for toluene (3, 26) and its cause is well speculated in (3, 6, 27). Current densities of up to 0.7 A cm-2 at 65 mass % of fuel in nitrogen were observed, which is comparable to 55% toluene current density (3).
Performance degradation of Cu-ceria SOFCs was observed for both the Pennsylvania crude oil as well as JP-8 Plus jet fuel after about 30 hours of operation, followed by a steady decline in performance (6). Carbon deposition was observed on the anode after the test and is believed to be the primary cause for the observed performance degradation.

**Waste Vegetable Oil Fueled SOFC**

The observed OCV for the direct oxidation of waste vegetable oil was 0.85-0.95 V, this being significantly less than that of hydrogen and similar to the obtained OCV for both jet fuel and crude oil testing described above. The SOFC with Cu-ceria anode was able to generate a current density up to 250 mA cm$^{-2}$.

Power generation with waste vegetable oil showed similar degradation behavior to the crude oil and jet fuels mentioned above. After approximately 30 hours of stable voltage, performance degradation was observed (7). This process was shown to be reversible with nitrogen purging.

Significant carbon deposition was observed as a result of operation of SOFC with Cu-ceria anode with unreformed waste vegetable oils. As there were only trace amounts of sulfur in the fuel, it was assumed that performance degradation was mainly due to coking. However, this degradation was found to be fully reversible by nitrogen flushing at operational temperature.
**Ethanol-Water Blend Fueled SOFC**

The OCV values measured for the ethanol-water blend were compared to those obtained with hydrogen nitrogen gas mixture (1:1 by flow rate), and these values are listed in Table 1-1.

**Table 1-1.** Open circuit potential (OCP) in volts of SOFC operated with different fuel blends as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>650 °C</th>
<th>750 °C</th>
<th>850 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂:N₂ (1:1)</td>
<td>0.954 V</td>
<td>0.959 V</td>
<td>0.957 V</td>
</tr>
<tr>
<td>Ethanol-Water (1:1)</td>
<td>0.692 V</td>
<td>0.902 V</td>
<td>0.951 V</td>
</tr>
</tbody>
</table>

The OCV measured for higher temperatures agree with those reported in Ref. (13) for both ethanol water blend as well as hydrogen operating on a similar test apparatus at 800 °C. The OCV values for the ethanol-fueled SOFC approach the values obtained with hydrogen as the temperature is increased, which suggests more complete internal reforming of ethanol at higher temperatures.

The electrochemical impedance spectra were taken in a region of high frequencies for the SOFC operating with the ethanol-water blend under open circuit conditions at different temperatures. From the obtained EIS data presented the ohmic resistances of the cell were determined to be 39.1 and 31.4 Ω at 650 and 750 °C, respectively. The observed drop in the total cell resistance is probably due to the higher conductivity of the YSZ electrolyte. The polarization resistance of the SOFC was determined to be approximately 25 and 15 Ω at 650 and 750 °C, respectively. This tendency of decreasing polarization resistance with increasing temperature probably indicates faster kinetics and transport of
ethanol at the anode, which can be in part a result of internal reforming of ethanol to H$_2$-containing gaseous mixture.

**Bio-diesel Fueled SOFC**

Figure 1-1 shows the voltage–current density (V-I) and power density–current density (P-I) performance curves for the fuel cell with Cu-ceria anode fueled with biodiesel at 700 °C. Data were obtained at three different fuel supply rates 1, 5, and 20 μl min$^{-1}$. Open circuit voltages (OCV) were close to 0.9 V, again with a higher supply rate, giving rise to marginally higher OCV. The OCV values obtained with biodiesel were substantially lower than those for H$_2$ but similar to those reported for jet fuels, Pennsylvania crude oil (6) and waste vegetable oil (7). The maximum power density also varied with fuel supply rate, and 102 mW cm$^{-2}$ was obtained with the highest fuel supply rate. It is noted that at a low flow rate (1 μl min$^{-1}$), the power density displays a plateau at approximately 35 mWcm$^{-2}$. 
Figure 1-1. Potential and power density vs. current density at three different flow rates for Cu-ceria fuel cell at 700°C.

Figure 1-2 presents the V–I and P–I performance curves for a SOFC with Rh-ceria anode fueled with biodiesel at 700 °C and at the same three supply rates 1, 5, 20 μl min⁻¹. OCVs were in the range of 0.8 to 1.1 V, with the maximum voltage being closer to the Nernst potential.
Figure 1-2. Potential and power density vs. current density at three different flow rates for Ce-Rh fuel cell at 700 °C.

The maximum power densities were also significantly higher than those shown in Figure 1-1 for the corresponding fuel supply rates. The relatively high power density of 250 mW cm\(^{-2}\) was unexpectedly obtained at fuel supply rate of 1 μl min\(^{-1}\). The better performance at lower supply rate might be associated with the rhodium catalysis that works most efficiently in less concentrated fuel. We assume that rhodium addition enhanced the conversion of the biodiesel fuel into H\(_2\) and CO in the reforming process and favored quicker oxidation of these gaseous fuels. In addition the noble metal catalyst is reported to improve gas diffusion (28) and hence to reduce concentration polarization. As a result, higher voltage and power densities were obtained with Rh-ceria anode.

The long-term performances of the two fuel cells based on Cu-ceria and Rh-ceria anodes working on bio-diesel fuel are exhibited in Figures 1-3 and 1-4, respectively. The
liquid fuel was injected into the anode compartment at a rate of 1μl min$^{-1}$ in both cases. This fuel generated electric power of about 35 mW cm$^{-2}$ on the Cu-ceria fuel cell (Fig. 3).

![Graph showing voltage and current density vs. time for Cu-Ce SOFC on Biodiesel](image)

**Figure 1-3.** Potential and current density vs. time for Cu-ceria fuel cell at 700 °C.
The generated electric power showed a steady decline in both voltage and current density. In contrast, the electric power of about 230 mWcm$^{-2}$ was generated on the Rh-ceria fuel cell steadily over 45 hours. Both the voltage and the current density did not exhibit significant oscillations. The prolonged stability of power generation observed in this fuel cell may be explained as follows. Firstly, the fuel supply rate was relatively low; therefore, there was less carbon deposition, which is a major cause of anode deactivation (7). Second, Rh is a more effective oxidation catalyst, so more H$_2$O and CO$_2$ were generated in the process that assisted with diluting the fuel and also reduced carbon deposition.
Conclusions

A variety of alternative fuels have been tested in SOFC, and their potential for direct oxidation was confirmed. SOFCs with Cu-ceria anodes have generated power with minimal degradation when operating with nitrogen diluted Pennsylvania crude oil, JP-7 and JP-8 Plus jet fuels, and biodiesel. Performance degradation of the SOFC operated with waste vegetable oil as fuel was found to be reversible with nitrogen flushing. Ethanol-water blend (1:1) has been tested as alternative fuel for direct oxidation in SOFC with a Ni-YSZ anode. As the operating temperature increased from 650 to 850 °C, the open circuit potentials obtained with the ethanol-water blend gradually approached the values obtained with H2/N2 blend as fuel and were almost equal at 850 °C. This probably indicates that at temperatures around 850 °C, internal reforming of ethanol maybe close to 100%, although the exhaust gas analysis would be necessary to confirm this assumption. Both ohmic and polarization resistances of the SOFC operated with the 1:1 ethanol-water blend were shown to decrease with temperature in a short term test, showing more favorable kinetics for internal reforming reaction for ethanol at higher temperatures. However, this study is being continued to provide a detailed EIS characterization on a longer time scale, when the balance between possible degradation processes and internal reforming kinetics will need to be optimized by tuning temperature and fuel composition. The degradation tests with biodiesel-fueled SOFCs indicated that the Rh-ceria anode provides more steady operation (over 45 hours) compared to Cu-ceria anode at relatively low fuel supply rates.
Chapter 1 References


Chapter 2

Solid Oxide Fuel Cell Fueled by Diesel Reformate and Anaerobic Digester Gas


Preface to Chapter 2

Chapter 2 demonstrates the ability to operate an integrated SOFC fuel reformation system as well as to take in-situ impedance spectra of the system. By extending the range of alternative fuels utilized in this study from the unreformed liquid hydrocarbons of Chapter 1 to commercial diesel steam reformate and a model scrubbed anaerobic digester gas, the performance and impedance contributions are analyzed.

This study was a collaborative effort with the fuel reformation team under Dr. Song to generate electricity using an integrated commercial diesel steam reformation system and SOFC, as well as to generate power from a model of cleaned anaerobic digester gas from the Penn State University Waste Water Treatment Center.
Abstract

A solid oxide fuel cell with a nickel-yttria stabilized zirconia cermet anode and a porous lanthanum strontium manganite cathode was used to generate electrical power directly from anaerobic digester gas and commercial diesel steam reformate. A diesel reformer was combined with the solid oxide fuel cell system in a single operating unit to convert diesel to electricity. To model anaerobic digester gas (ADG), a fuel gas mixture was prepared based on analytical data on real ADG from a local water cleaning facility. Electrochemical performance characterization involved power generation across a variety of external loads to characterize open circuit potential, maximum power densities and limiting current densities. The effects of anode poisoning from of sulfur compounds and their removal from the ADG fuel were studied.

Introduction

Electrochemical oxidation of fuels is a highly sought after approach to electrical power generation as it is removed from the thermodynamic efficiency limitations imposed by a traditional combustion or heat engine. Solid oxide fuel cells (SOFC) are considered especially promising energy conversion systems for stationary and potentially portable power generation due to their fuel flexibility and high energy efficiency [1]. SOFC have been shown to generate electrical power by direct electrochemical oxidation of a variety of fuels, from hydrogen, CO, and natural gas to heavier hydrocarbon fuels [2-6]. However, this technology still has limitations with respect to durability of performance and mitigation of undesirable contaminations (i.e. poisoning by impurities,
carbon deposition etc.). New efficient cleaning and reforming technologies are apparently needed to pre-treat the liquid and gas hydrocarbons in order to use those fuels in SOFC directly and reliably for commercially feasible periods of time.

Usually, steam reforming research and fuel cell tests have been done independently although the two processes are intimately related. In this study we attempt to build an integrated SOFC and steam reforming system to generate stable electrical power from alternative fuels. One of the main objectives of this research is to develop new fuel processing approaches for using selected alternative and renewable fuels – anaerobic digester gas (ADG) and commercial diesel fuel (with 15 ppmw sulfur) – in a laboratory scale solid oxide fuel cell power generation systems.

**Experimental System and Procedure**

**Fuel Chemistry, Cleaning and Reforming**

A series of performance tests were carried out to characterize the performance of solid oxide fuel cells fueled by a steam-reformed commercial diesel and anaerobic digester gas.

The commercial diesel steam reformate was prepared in the following manner. The catalyst used in the steam reforming process was 10% Ni, 5% Fe and 5% K (by weight) supported on Al₂O₃. The catalyst was prepared by wet impregnation of Al₂O₃ with Ni(NO₃)₂, Fe(NO₃)₃ and K(NO₃). Approximately, 1 g of catalyst with particle sizes of 18-35 mesh (0.5-1 mm) was placed in the center of a stainless steel tube (0.54 inch
o.d., 0.375 inch i.d., 24 inch long) with the rest of the tube being packed with α-alumina beads. The reforming reaction was performed at 800 ºC. Prior to the reactions, the catalysts were reduced by UHP hydrogen (20 ml/min) at 800 ºC. Both water and fuel were pumped via HPLC pumps through a pre-heater and then into the reactor at volumetric flow rates of 4.08 and 1.38 mL/h, respectively, for a steam-to-carbon molar ratio (S/C) of 3:1. The fuel employed in this study was commercially available diesel with 15 ppmw (parts per million by weight) sulfur. The composition of the commercial diesel reformate was calculated to be approximately 70% H2, 20% CO, 5% CO2, 2% CH4, 3% H2O and less than 5 ppm sulfur (all percent by weight) [7].

The anaerobic digester gas used in these experiments was prepared from 55% CH4 and 45% CO2 by volume. This composition is based on analysis of anaerobic digester gas generated at the Penn State Waste Water Treatment Center after sulfur removal [7].

Hydrogen gas was used as a reference fuel tested before and after the runs with ADG and commercial diesel. Hydrogen was also used to pre-operate and to condition the fuel cells in the furnace.

**Solid Oxide Fuel Cell Materials and Preparation**

The solid oxide fuel cells used in these experiments were NextCell-B button cells with 1.256 cm² active area (Fuel Cell Materials). The SOFC membranes in these cells were 150 μm dense yttria stabilized zirconia (YSZ), 8 mol.% yttria. The anode layer was a porous 50 μm nickel-YSZ cermet, and the cathode layer was a porous 50 μm lanthanum
strontium manganite (LSM).

The SOFCs were prepared for testing in the following manner. 99.99% purity gold wire (Alfa-Aesar), used as current collector, was adhered to both the anode and cathode sides of the button cell by covering the wire and electrode with a silver paste. The SOFC was then pasted onto an alumina tube using Armeco ceramabond, alumina paste, with the anode side facing into the tube.

Test System and Equipment

During operation and heat-up phases the SOFC was mounted vertically, anode side up, in a Barnstead Thermolyne tubular furnace. Both the hydrogen and anaerobic digester gas bubble-humidified at 25 °C. Diesel steam reformate was already saturated with water vapor at 25 °C at the outlet, therefore no additional humidification was required. The cathode was exposed to atmospheric air fed and was not humidified. The assembled SOFC system was heated at a rate of 5 °C min-1 to 900 °C. Flow rates of all fuels were maintained at approximately 100 cm³ min⁻¹ (at standard temperature and pressure conditions).

The diesel steam reforming system was integrated directly with the SOFC system, as shown in Figure 2-1.
**Figure 2-1.** Schematic of the integrated commercial diesel steam reformer and solid oxide fuel cell system.

**Electrochemical Testing**

The electrical equipment used to characterize fuel cell performance was a Solartron Analytical 1470-E and 1252-A, Potentiostat and frequency response analyzer. Each data set reported here is taken using the same fuel cell and without any thermal cycling. Hydrogen tests were carried out before and after each alternative fuel test. The performance and power generation were studied by maintaining a controlled external electric load using a Solartron Analytical 1470-E Potentiostat with Cell Test software.
Each data point reported represents the steady state voltage and current reached after allowing the SOFC to generate power in an external electric load for 60 seconds.

Results and Discussion

The performance of solid oxide fuel cells fueled by anaerobic digester gas and commercial diesel steam reformate were compared to hydrogen gas. Hydrogen testing carried out before and after each alternative fuel test showed repeatable voltage and current density behavior. The performance and power curves presented in Figures 2-2 and 2-3 were generated by allowing the fuel cell to reach a steady state performance across a series of decreasing external electric loads.

The performance curves in Figure 2-2, electric potential vs. current density, demonstrate a typical behavior of hydrogen in Ni-YSZ anode SOFCs: an open circuit potential was recorded at 1.0 V, and a limiting current density extrapolated to approximately 1.30 A cm⁻². Hydrogen testing was repeated before and after each alternative fuel test and showed no observable degradation; a 15 min. hydrogen purge was used prior to each hydrogen test. The electric potential and current density performance of commercial diesel steam reformate was somewhat lower than that with hydrogen, which was expected. The curve obtained with the ADG was close to the diesel curve at higher potentials, but showed deviation towards lower current at higher loads and indicated some limiting current density at approximately 0.5 A cm⁻².
Figure 2-2. Performance curve (cell potential vs. current density) of SOFC fueled by hydrogen, anaerobic digester gas and diesel reformate at 900 °C.

The power generation behavior demonstrated in Figure 2-3 indicates the maximum power density generated by hydrogen fuel in the SOFC system at 0.325 W cm-2 which is observed at 0.65 A cm-2 and 0.5 V (or approximately 50% of the open circuit potential).
Figure 2-3. Electric power generation curve (power density vs. current density) of SOFC fueled by hydrogen, anaerobic digester gas and diesel reformate.

**Anaerobic Digester Gas**

The electric potential and current density performance of model anaerobic digester gas shown in Figure 2-2 demonstrates an open circuit potential of 0.825 V and a limiting current density of 0.5 A cm\(^{-2}\).

A maximum power density from the ADG fueled SOFC of 0.14 W cm\(^{-2}\) is observed at 0.375 A cm\(^{-2}\) and 0.4 V, as shown in Figure 2-3. Anaerobic digester gas shows significantly reduced limiting current density and maximum power
density when compared to hydrogen. This behavior is believed to result from the significant content of inert CO2 in the fuel. However, performance of ADG fueled SOFCs at current densities below 0.20 A cm-2 showed comparable behavior to the diesel reformate.

The impedance spectra generated by hydrogen and anaerobic digester gas fueled SOFCs are taken from the integrated system design. These impedance spectra are overlaid in Figure 2-4. The increase in magnitude of impedance in anaerobic digester gas is primarily a result of low frequency impedance growth, however some increase is seen in the high frequency arc as well.
Figure 2-4. Impedance spectra generated by hydrogen fueled and anaerobic digester gas fueled SOFC at 900 °C with air fed anode. The sweeps are run form 50 kHz (left) to 10 Hz (right).

Commercial Diesel Steam Reformate

The reformate generated from a 3:1 water to commercial diesel steam reformation was shown to be a viable fuel for SOFCs. The open circuit potential observed from diesel reformate was 0.9 V and the limiting current density is extrapolated to be approximately 0.9 A cm⁻². The maximum power density observed in commercial diesel stem reformate SOFC is 0.20 W cm⁻²; this occurs at 0.45 A cm⁻² and 0.444 V.

Table 2-1, below, compares the performance data of each of the fuels tested. Data includes limiting current density and maximum power density observed at 900 °C, Hydrogen testing was carried out between each fuel tested to verify repeatability and accuracy.

Table 2-1. Comparison of SOFC performance parameters for different types of alternative fuels.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Limiting Current Density, A cm⁻²</th>
<th>Maximum Power Density, W cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1.30</td>
<td>0.325</td>
</tr>
<tr>
<td>Commercial Diesel Reformate</td>
<td>0.90</td>
<td>0.20</td>
</tr>
<tr>
<td>Anaerobic Digester Gas</td>
<td>0.50</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Due to the hydrogen rich nature of the commercial diesel reformate generated in the integrated steam reformer SOFC system tested in these experiments, electrical
potential and current density performance is similar to pure hydrogen, (with approximately a 10-20% reduction). Based on the power density measurements, current densities up to 0.5 A cm$^{-2}$ would be most feasible for performance of diesel reformate fueled SOFCs without significant efficiency losses.

**Conclusion**

The performance of solid oxide fuel cells fueled by commercial diesel steam reformate and anaerobic digester gas was measured in this study and compared to hydrogen as a baseline fuel. These fuels are generally considered alternative in electrochemical (non-combustion) energy conversion systems, and the results of this study demonstrate the feasibility and limitations of utilizing those in solid oxide fuel cells.

A comparison of the limiting current density and maximum power density achieved using a single button style SOFC on each fuel is presented in Table I. These results indicate that current densities below that of the maximum power density, solid oxide fuel cells fueled by commercial diesel steam reformate and desulfurized anaerobic digester gas can be used to generate electrical power with only moderate performance losses compared to hydrogen.
Chapter 2 References


Chapter 3

Sn-Pb Liquid Metal Anode Solid Oxide Fuel Cell Fueled by Coal


Preface to Chapter 3

Chapter 3 details a preliminary investigation into the development of a functional coal-fueled liquid metal anode SOFC. Extending the range of fuels available in SOFCs to include unreformed solid hydrocarbons may provide a drastic increase in chemical to electrical energy conversion efficiency compared to traditional heat engine based electricity generation. Development of a novel anode design is required to directly oxidize solid hydrocarbons electrochemically in a SOFC. This advancement could provide a vast supply of high efficiency electrical power in future power generation facilities.

The work reported in this chapter addresses the development and analysis of a novel anode design, utilizing several anode materials, for the direct consumption of hydrogen and coal in a SOFC. This research employs some unconventional methodology and materials as it was not directly funded and utilized only excess materials available in the laboratory.
Abstract

A Sn-Pb liquid alloy, Bi liquid metal, and Sn-Pb-Bi liquid alloy are investigated as potential anodes for a solid oxide fuel cell (SOFC) powered directly by coal. Power generation from direct oxidation of pulverized coal is demonstrated in a Sn-Pb liquid metal anode SOFC (LMA-SOFC) design. The tests are carried out at 900 °C under ambient pressure with air-fed cathode. The open circuit potentials (OCP) of the SOFC with nitrogen fed liquid Sn-Pb anode (0.824 V) and Bi liquid metal anode (0.408 V) are similar to the expected values for the respective metal oxidation to SnO$_2$(s) and Bi$_2$O$_3$(s). An observed OCP of 0.997 V is generated by a hydrogen (3 % H$_2$O) fueled liquid Sn-Pb anode SOFC, indicating a direct electrochemical reaction between H$_2$(g) fuel and O$_2$(g) oxidizer. The Sn-Pb LMA-SOFC, while under inert N2(g), is fed a 60-mesh bituminous coal powder directly to the surface of the liquid metal anode, which results in a sharp increase in OCP and allows the SOFC to generate power from subsequent coal injections. No direct electrochemical reaction is observed between hydrogen and oxygen in the Bi liquid metal anode or Sn-Pb-Bi liquid metal anode SOFC.

Introduction

Fuel cell technologies provide a means of producing electrical energy from fuel oxidation with high efficiency and lower carbon dioxide emissions. Many fuel cell designs (proton exchange membrane, alkaline, phosphoric acid) are limited to hydrogen or methanol fuels. Solid oxide fuel cell (SOFC) designs offer to utilize a wide range of hydrocarbon fuels for electrical power generation [1-5]. Fuels commonly used in SOFCs
are light hydrocarbon gasses (e.g. natural gas, methane, carbon monoxide, propane, hydrogen) as well as a wide range of heavier liquid hydrocarbons that internally reform within the SOFC (e.g. diesel fuel, waste vegetable oil, bio-diesel, jet fuels, crude oil, a variety of alcohols) [6-9]. Solid fuel sources such as coal and biomass have been externally reformed and used as SOFC fuel source [10]. However, recent developments in SOFC anode design, specifically liquid metal anode solid oxide fuel cells (LMA-SOFC), have been considered as a means to generate electrical power from the oxidation of solid hydrocarbons [11-13].

The reaction mechanism that is believed to proceed in LMA-SOFCs is as follows: the electrochemical reduction of O$_2$ from air to O$^{2-}$ ions occurs at the cathode; the oxygen ions are then conducted through a dense ceramic electrolyte membrane; the O$^{2-}$ ions then electrochemically oxidize the liquid metal anode to a metal oxide freeing two high potential electrons that dissipate their power in an external circuit before returning to the cathode for O$_2$ reduction; finally the addition of fuel to the liquid metal anode initiates a chemical reduction of metal oxide (regenerating the liquid metal anode material) and chemical fuel oxidation (producing the fuel oxidation products) [3,4,14-22]. To date most LMA-SOFC studies have been focusing on the oxidation of hydrogen fuel, jet fuels, and bio-diesel in a liquid Sn anode SOFC [8,9,21]. A conceptual schematic of the reaction mechanism within a hydrogen and graphite fueled liquid Sn anode SOFC is displayed in Figure 3-1.
This previously proposed mechanism can be represented for the hydrogen-oxygen reaction by the following electrochemical diagram:

\[
\begin{align*}
H_2(g) + \frac{1}{2} \text{SnO}_2(s) &\rightarrow \frac{1}{2} \text{Sn}(l) + H_2O(g) \\
C(s) + \text{SnO}_2(s) &\rightarrow \text{Sn}(l) + CO_2(g)
\end{align*}
\]

This electrochemical reaction is believed to result from the following half-reactions:

\[
\begin{align*}
\frac{1}{2} \text{Sn}(l) + O^{-2} (\text{YSZ}) &\rightarrow \frac{1}{2} \text{SnO}_2(s) + 2 \text{e}^{-} \text{ (anodic)}
\end{align*}
\]

\[1\]
\[(1/2) \text{O}_2(\text{g}) + 2 \text{e}^- \rightarrow \text{O}^{2-} \text{(YSZ)} \text{ (cathodic)} \] \[4\]

Then the chemical reduction of hydrogen occurs through the reaction:

\[\text{H}_2(\text{g}) + (1/2) \text{SnO}_2(\text{s}) \rightarrow \text{H}_2\text{O}(\text{g}) + (1/2) \text{Sn(1)} \] \[5\]

The electrochemical oxidation of solid graphite, C(s), in LMA SOFC is predicted to occur based on the following electrochemical diagram:

\[\text{C}(\text{s}), \text{CO}_2(\text{g}) | \text{Sn(l)}, \text{SnO}_2(\text{s}) | \text{YSZ} | \text{LSM} | \text{O}_2(\text{g})\]

In this case, the net fuel oxidation reaction is:

\[(1/2) \text{C(s)} + (1/2) \text{O}_2(\text{g}) \rightarrow (1/2) \text{CO}_2(\text{g}) \] \[6\]

and the overall electrochemical reaction remains:

\[(1/2) \text{Sn(l)} + (1/2) \text{O}_2(\text{g}) \rightarrow (1/2) \text{SnO}_2(\text{s}) \] \[7\]

Reaction \[7\] results from the electrochemical half-reactions:

\[(1/2) \text{Sn(l)} + \text{O}^{2-} \text{(YSZ)} \rightarrow (1/2) \text{SnO}_2(\text{s}) + 2 \text{e}^- \text{ (anodic)} \] \[8\]

\[(1/2) \text{O}_2(\text{g}) + 2 \text{e}^- \rightarrow \text{O}^{2-} \text{(YSZ)} \text{ (cathodic)} \] \[9\]

Finally, the chemical reduction of carbon occurs as:

\[(1/2) \text{C(s)} + (1/2) \text{SnO}_2(\text{s}) \rightarrow (1/2) \text{CO}_2(\text{g}) + (1/2) \text{Sn(l)} \] \[10\]

**Standard Electrode Potential and the Nernst Equation**

The maximum electrical potential (voltage) generated by an electrochemical system, the equilibrium electrode potential \(E_{\text{eq}}\), can be determined if the standard Gibbs energy for overall electrochemical reaction \(\Delta_rG^\circ\), the activities of all reactant and product species \(i (a_i)\), the charge number of the electrochemical reaction \(z\), and the
stoichiometric coefficients of all species \(i (v_i)\) are known. These parameters are accounted for in the well-known Nernst equation as follows:

\[
E_{eq} = E^o + \frac{RT}{zF} \sum v_i \ln a_i
\]  

In Equation 11, \(E^o = -\Delta_r G^o/(zF)\), where \(E^o\) is the standard electrode potential of the reaction, \(R\) is the molar gas constant, 8.314 J mol\(^{-1}\)K\(^{-1}\); \(F\) is Faraday’s constant, 96485 C mol\(^{-1}\), \(T\) is absolute temperature. In an ideal case the OCP will be equal to the Nernstian value, but in reality can be lower due to a number of reasons usually related to reversibility of the process at the cell electrodes.

**Liquid Metal-Metal Oxide Redox Couples and Fuel Oxidation**

In a common electrochemical system two simultaneous half-reactions occur in a manner that separates the reactions physically while connecting them ionically through an ion conductive membrane and electronically through the outer electrical circuit. In order for the electrochemical system to generate power, the ionic and electronic paths must be distinct and well defined [5].

The oxidation of metals is generally a spontaneous chemical reaction, meaning the Gibbs energy1 of the reaction is negative. A reaction with a negative Gibbs energy can be used to generate electric power in a galvanic electrochemical cell [5]. The standard electrode potential and standard Gibbs energy of the metal oxidation reaction and fuel oxidation relevant to this study are given in Table 3-1. These values were calculated at 900 °C using HSC Chemistry 6.12 [23].
Table 3-1. Standard thermodynamic properties of liquid metal and fuel oxidation redox couples. Standard Gibbs Energy ($\Delta_rG^\circ$), charge number ($z$), and standard equilibrium potential ($E^\circ_{eq}$) are calculated at 900 °C using HSC Chemistry 6.12 [23]

<table>
<thead>
<tr>
<th>Oxidation Reaction</th>
<th>$\Delta_rG^\circ$ (kJ mol$^{-1}$)</th>
<th>$z$</th>
<th>$E^\circ_{eq}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(l) + (½) O$_2$(g) $\leftrightarrow$ SnO(l)</td>
<td>-162.751</td>
<td>2</td>
<td>0.843</td>
</tr>
<tr>
<td>Sn(l) + O$_2$(g) $\leftrightarrow$ SnO$_2$(s)</td>
<td>-338.464</td>
<td>4</td>
<td>0.877</td>
</tr>
<tr>
<td>Pb(l) + (½) O$_2$(g) $\leftrightarrow$ PbO(l)</td>
<td>-102.691</td>
<td>2</td>
<td>0.532</td>
</tr>
<tr>
<td>Bi(l) + (¾) O$_2$(g) $\leftrightarrow$ (½) Bi$_2$O$_3$(s)</td>
<td>-127.309</td>
<td>3</td>
<td>0.440</td>
</tr>
<tr>
<td>H$_2$(g) + (½) O$_2$(g) $\leftrightarrow$ H$_2$O(g)</td>
<td>-183.120</td>
<td>2</td>
<td>0.949</td>
</tr>
<tr>
<td>C(s) + O$_2$(g) $\leftrightarrow$ CO$_2$(g)</td>
<td>-396.039</td>
<td>4</td>
<td>1.026</td>
</tr>
</tbody>
</table>

For fuel oxidation in SOFC systems, such as that used in this study, concentrations of reactants and products can deviate from unit activity. However, this deviation will not significantly change the equilibrium electrode potential, $E^\circ_{eq}$, until a component activity is extremely small or large. We are not expecting this case in our studies.

In the SOFC system tested in this study, a humidified hydrogen and nitrogen blend is supplied to the anode at 900 °C. The partial pressures of nitrogen, hydrogen, and water vapor were 0.5, 0.485, and 0.015 bar, respectively, based on feed flow rates, and oxygen partial pressure at the cathode was 0.21 bar. For these calculations activities are assumed to be equal to partial pressures. When these values are substituted into the Nernst equation (Equation 11), along with the standard electrode potential from Table 1, the theoretical OCP is calculated as 1.085 V.
A similar calculation could be carried out for coal, however some assumption regarding coal’s chemical equivalence to graphite would need to be made, and the concentration of CO$_2$ at the anode and the activities of species involved in the reactions would need to be specified.

**Experimental System and Procedure**

**Solid Oxide Fuel Cell Preparation**

The solid oxide fuel cells modified and tested in these experiments are NextCell$^\text{TM}$ electrolyte-supported button cells (Fuel Cell Materials). The membrane electrode assembly (MEA) is supported by a dense 150-micron YSZ (8 % yttria by mol in zirconia) membrane, supporting a porous 50-micron Ni-YSZ anode, and a porous 50-micron LSM cathode.

The MEAs are prepared for testing according to the following procedure. A nickel gauze current collector, 40 mesh woven from 0.13 mm diameter wire (Alfa Aesar), is fixed to the anode active area (1.23 cm$^2$) using nickel ink. The nickel ink (NexTech Materials Ltd.) consisted of nickel powder in terpineol, 2-(4-Methyl-1-cyclohex-3-enyl) propan-2-ol solvent. The MEA is placed in a furnace and heated to 900 °C in 10 °C min$^{-1}$ increments and, then, cooled down at a similar rate for sintering. Next, the button cell is mounted on an open-end 13 mm. inner diameter alumina tube, with anode side facing inside the tube, using high-temperature alumina cement (Aremco Ceramabond$^\text{TM}$ 552 High Temperature Ceramic Adhesive). The LSM paste (NexTech Materials Ltd.) consists
of lanthanum oxide, manganese oxide, and strontium oxide in terpineol vehicle. A schematic of the fully assembled SOFC sample is shown in Figure 3-2. Though it is known that nickel and tin can alloy at 900 °C, no nickel was observed in energy-dispersive X-ray spectrum taken of the Sn-Pb-Bi anode and, therefore, is not assumed to participate in the catalytic process.

![Figure 3-2. Membrane electrode assembly of LMA-SOFC; during operation “anode chamber” is filled with humidified nitrogen, humidified nitrogen-hydrogen blend, or coal under humidified nitrogen.](image)

**Liquid Metal Anode Materials**

In this study three compositions of LMA are tested: first a 1:1 Sn-Pb mixture, second pure Bi, and finally a Pb-Sn-Bi mixture. These materials are chosen because of our interest using an alloy as LMA instead of a pure metal.

The Sn-Pb ingot is prepared by purification of Luco wire solder 50/50 tin lead with rosin core. The Sn-Pb mixture is purified by a four-step process. First, a 5 cm section of the material is heated under an air environment in a crucible with a propane
flame allowing many impurities to burn off while the metal mixture is melted; next, the liquid metal is poured off, only taking the first pour of liquid metal, onto a Pyrex watch glass (leaving behind much of the impurities); this step provides a more lustrous product. Finally, to further purify the sample, the above steps are repeated. The purity of this sample is verified by a series of energy disperse X-ray spectra and backscattered electron imaging tests. These results show that the sample is pure to greater than 99 % lead and tin, and no significant contaminants are present. A backscattered electron image of the Sn-Pb alloy used in the LMA-SOFC is shown in Figure 3-3. Copper, carbon, and nitrogen are all seen in amounts less than 0.5 %, by weight on the surface of the anode. The Bi metal used in the experiments is 325 mesh 99.5 % purity metal powder (Alfa Aesar). In preparing the Sn-Pb-Bi anode, the bismuth powder is added to the above-described 1:1 Sn-Pb alloy to produce the 50 % Bi, 25 % Sn, 25 % Pb mass ratio. The analysis carried out after cell operation shows that the predominant oxide formed in the alloy (when allowed) was tin dioxide, SnO$_2$(s).
Figure 3-3. Backscattered electron image of the Sn-Pb alloy used as anode material in the LMA-SOFC.

The alloys are introduced to the SOFC in the following manner. In the case of the Sn-Pb alloy, the purified ingot is placed on top of the anode side of the fully assembled cell. In the case of Bi anode, 2.5 g of Bi powder is added atop the anode side of the cell. Once the Bi tests are complete, a second similar Sn-Pb alloy ingot is added onto the liquid Bi anode and allowed to melt and mix with the Bi to form the Sn-Pb-Bi alloy.
Coal Fuel Samples

The 60-mesh coal powder sample used as fuel in the LMA SOFC is provided by the Coal Utilization Laboratory (Earth and Mineral Sciences Energy Institute, Penn State University). A series of three proximate and ultimate analyses are carried out to determine the composition of the coal sample. Based on the averaged results of the proximate analysis, the moisture composition is 2.86 % (as received). Using a dry basis, the following compositions are measured (mass %): 5.36 % ash, 32.54 % volatiles, and 62.09 % fixed carbon. Based on the averaged results of the ultimate analysis, using a dry basis, the coal contains (mass %): 89.25 % carbon, 5.45 % hydrogen, 3.08 % oxygen, 1.49 % nitrogen, and 0.73 % sulfur.

Test Procedure and Equipment

A Solartron Analytical 1470E Cell Test System Potentiostat and Solartron Analytical 1252A Frequency Response Analyzer controlled by Cell Test software are used to control all electrical testing carried out in this study. An Arbin Instruments Fuel Cell Test Station controls the system’s flow rates, pressures, and humidification. A Barnstead Thermolyne 21100 tubular furnace is employed in this study to control the operating temperature.

All experimental tests are carried out in a vertically oriented tubular furnace with a tube-mounted SOFC inserted vertically with the anode facing upwards. The experimental temperature is maintained at 900 °C and ambient air is used for SOFC cathode. The heating of the fuel cell system is carried out from room temperature to 900}
°C at a rate of 10 °C min⁻¹ under 57 cm³ s⁻¹ nitrogen anode flow. These conditions are maintained for the entire duration of the electrochemical metal–metal oxide redox couple tests. The linear potential sweeps under nitrogen hydrogen 1:1 blend are carried out under 57 cm³ s⁻¹ N₂ co-fed with 57 cm³ s⁻¹ humidified hydrogen (saturated at 25 °C). The coal power generation and OCP tests are carried out with 57 cm³ s⁻¹ N₂ flow.

To investigate the electrochemical behavior of the liquid metal alloys and their corresponding oxide, a series of experiments are carried out on each anode material. The OCP measurements determine the electric potential at which no net-current is flowing between the electrodes. The OCP of each anode material is determined by multiple linear potential sweeps. The OCP for each electrode material is measured under both inert N₂ and while fueled by H₂ separately.

Power generation from the direct electrochemical oxidation of coal in a liquid tin-lead alloy anode SOFC is analyzed. While maintaining a nitrogen anode environment, a 0.05 g sample of coal is directly poured onto the liquid anode surface, and the response of the cell OCP is monitored. Then a power generation test is carried out by applying an external load of 5 Ω to the coal fed liquid metal anode SOFC. During this phase 2 subsequent injections of coal are made while monitoring produced current and voltage.

**Results and Discussion**

The results of a series of electrochemical tests carried out on three liquid metal anodes are presented here. The LMA tested are Sn-Pb alloy, Bi metal, and Sn-Pb-Bi alloy. All tests are carried out at 900 °C with an air fed cathode at ambient pressure.
Sn-Pb Liquid Metal Anode Solid Oxide Fuel Cell

The OCP of the liquid Sn-Pb anode SOFC under nitrogen atmosphere is determined by a series of linear potential sweeps. In this experiment the potential between the electrodes is swept from 1.3 to 0.3 V and back for five complete cycles, each at a rate of 16.7 mV s\(^{-1}\). The linear potential sweep curves generated from the potential sweeps of the Sn-Pb LMA-SOFC under pure nitrogen are shown in Figure 3-4. The OCP of the Sn-Pb LMA-SOFC anode SOFC under nitrogen is measured to be 0.824 V; this is observed when the net current is equal to zero.

**Figure 3-4.** Linear potential sweep data for Sn-Pb LMA-SOFC at 900 °C under an inert nitrogen anode environment (OCP is 824 mV).
The second series of linear potential sweeps with the Sn-Pb LMA-SOFC are performed while supplying the anode hydrogen and nitrogen 1:1 blend humidified at 25 °C. In this experiment the potential between the electrodes is swept from 1.25 to 0.75 V, at a rate of 8.3 mV s\(^{-1}\), for 5 complete cycles. The OCP value of the system is observed to be 0.997 V. Figure 3-5 displays the performance of the Sn-Pb LMA-SOFC fueled by hydrogen as determined by a linear potential sweep.

![Graph showing linear potential sweep data for Sn-Pb LMA-SOFC at 900 °C, with a hydrogen-fueled anode (OCP is 997 mV).]

**Figure 3-5.** Linear potential sweep data for Sn-Pb LMA-SOFC at 900 °C, with a hydrogen-fueled anode (OCP is 997 mV).

Power generation from the electrochemical oxidation of hydrogen using a Sn-Pb LMA-SOFC while under hydrogen and nitrogen 1:1 blend humidified at 25 °C is
demonstrated by applying an external electronic load. In this experiment power generated by the SOFC is monitored in the potentiostatic mode by varying the external load to maintain a cell potential of 443 mV for 13 hours. The power density, which is product of the cell potential and the current density, generated by the Sn-Pb LMA-SOFC, is found to slightly decrease from 11.7 to 10.1 mW cm\(^{-2}\) over the 13 hour test.

Next, finely ground coal particles (>60 mesh) are directly supplied to the anode of the vertically positioned cell assembly (Figure 3-2), under a humidified nitrogen atmosphere. The OCP of the Sn-Pb LMA-SOFC during coal injections is monitored (Figure 3-6). In this experiment, prior to coal injection, the OCP of the Sn-Pb LMA-SOFC is observed to be about 600 mV. After a sample of 0.05 g of finely ground coal is fed to the surface of the anode under nitrogen, the OCP of the system rises sharply from 600 to 775 mV where it remains stable for over 10 minutes.
Figure 3-6. Coal-fueled Sn-Pb LMA-SOFC at 900 °C; OCP increases from a single 0.05 g coal injection to the anode surface while under nitrogen.

Power generation from electrochemical oxidation of coal using a Sn-Pb LMA-SOFC is demonstrated applying an external electronic load (Figure 3-7). In this experiment power density rises sharply with each coal injection. The power density resulting from direct coal oxidation on LMA-SOFC is measured on the order of 14 mW cm⁻².
Figure 3-7. Coal-fueled Sn-Pb LMA-SOFC at 900 °C; power generation resulting from the application of an external electronic load following the 0.05 g coal injection at OCP and two subsequent 0.05 g coal injections.

Bi Liquid Metal Anode Solid Oxide Fuel Cell

The OCP of the Bi LMA-SOFC while under nitrogen is determined by a series of linear potential sweeps. In this experiment the potential between the electrodes is swept from 0.0 to 0.8 V, at a rate of 13.3 mV s⁻¹, for 5 complete cycles. The OCP of the Bi LMA-SOFC is measured to be 408 mV. Further, The OCP of the Bi LMA-SOFC while under 1:1 hydrogen nitrogen blend is determined by a series of linear potential sweeps.
from 0.0 to 0.8 V, at a rate of 13.3 mV s\(^{-1}\), for 5 complete cycles. The OCP of the Bi LMA-SOFC under hydrogen is measured to be 424 mV.

**Sn-Pb-Bi Liquid Metal Anode Solid Oxide Fuel Cell**

For the Sn-Pb-Bi LMA-SOFC running under nitrogen, potential between the electrodes is swept from 0.0 to 0.8 V, at a rate of 13.3 mV s\(^{-1}\), for 5 complete cycles. In this case, the OCP of the SOFC is measured to be 223 mV. While operating under a humidified 1:1 hydrogen nitrogen blend, the OCP of the Sn-Pb-Bi LMA-SOFC is determined by a series of linear potential sweeps from 0.0 to 0.8 V, at a rate of 0.8 V min\(^{-1}\), for 5 complete cycles. The OCP of the Sn-Pb-Bi LMA-SOFC under hydrogen is found to be between 117 and 322 mV and does not show sufficient stability.

**Discussion**

This section compares the behavior and electrochemical performance of different liquid metal anode materials, under nitrogen and when fueled by hydrogen and coal.

**Sn-Pb Liquid Metal Anode Solid Oxide Fuel Cell**

The Sn-Pb LMA-SOFC under nitrogen demonstrates an OCP of 824 mV while under hydrogen demonstrates an OCP of 997 mV. These OCPs are only slightly less than the respective calculated standard electrode potential for the Sn/SnO\(_2\) system 0.877 V and hydrogen oxidation 1.085 V.
The OCP behavior measured under nitrogen indicated the Sn-Pb LMA-SOFC could readily oxidize and reduce Sn to SnO₂ when the anode is maintained in an inert environment. The OCP observed under hydrogen indicates a direct electrochemical reaction between the fuel and oxygen across both the YSZ membrane and the Sn-Pb LMA. The spontaneous galvanic reaction of the Sn-Pb LMA-SOFC under nitrogen is believed to be reversible Sn oxidation:

\[ \text{Sn(l)} + 2 \text{O}_2(\text{g}) \rightarrow \text{SnO}_2(\text{s}) \]  

[12]

The Sn-Pb LMA-SOFC is shown to generate stable electrical power from hydrogen for 13 hours with slight performance degradation. During the 13-hour power generation phase the power density decreases by 14%. The precipitation of a solid SnO₂ layer between liquid tin and YSZ has been demonstrated by Jayakumar and co-authors [11]. This oxide deposition is a possible explanation of the reduction in power density over the course of the experiment. The OCP behavior measured under hydrogen indicates that the Sn-Pb LMA-SOFC can readily oxidize hydrogen fuel. The OCP and stable power generation observed under hydrogen indicate a direct electrochemical reaction between the fuel and oxygen across both the YSZ membrane and the Sn-Pb LMA as:

\[ \text{H}_2(\text{g}) + (1/2) \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \]  

[13]

While the Sn-Pb LMA-SOFC is fed coal powder under nitrogen, the OCP showed an immediate increase to a new stable value. This jump in OCP indicates a direct electrochemical reaction between the air fed cathode and the coal on the surface of the LMA. When an external load is connected to the Sn-Pb LMA-SOFC fueled with coal, the SOFC system generates electrical power from direct electrochemical oxidation of coal on the LMA. Each successive coal injection shows greater power densities (Figure 3-5).
These results demonstrate that Sn-Pb LMA-SOFCs are feasible for use in coal-based power generation.

**Bi Liquid Metal Anode Solid Oxide Fuel Cell**

The Bi LMA-SOFC demonstrates an OCP of 408 mV while under a nitrogen environment. This OCP value is slightly less than the calculated standard electrode potential for the Bi/Bi2O3 couple, 440 mV. This correlation in OCP indicated that the Bi LMA-SOFC is electrochemically oxidizing and reducing Bi to Bi2O3 while under nitrogen. The electrochemical reaction of the Bi LMA-SOFC is believed to be:

$$2 \text{Bi(l)} + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{Bi}_2\text{O}_3(\text{l})$$

With hydrogen fuel, the Bi LMA-SOFC demonstrates an OCP of 424 mV. This value is not near the Nernst potential for hydrogen oxidation, 1.085 V. The slight increase of the OCP from the metal-metal oxide redox potential under nitrogen is believed to be a result of chemical Bi oxidation to Bi2O3 (not the desired electrochemical oxidation of hydrogen). Further investigation would be required to properly categorize Bi as an LMA material, however the results of this study do not demonstrate any feasibility of this material as a LMA for SOFCs.

**Bi-Sn-Pb Liquid Metal Anode Solid Oxide Fuel Cell**

The Sn-Pb-Bi LMA-SOFC showed unfavorable anodic behavior under both nitrogen or hydrogen feed. The OCP observed under nitrogen and hydrogen are 223 and
117 mV, respectively. These are less than respective Nernst potentials and do not indicate any promise from adding Bi to Sn-Pb LMA-SOFCs.

**Conclusions**

Based on the findings of this study, Sn-Pb is a promising LMA material for direct oxidation of coal and possibly other hydrocarbon fuels in SOFC systems. The electric power can be generated by direct electrochemical oxidation of coal, yielding an exhaust of undiluted carbon dioxide and steam. One significant conclusion that can be drawn from the observed OCP behavior in the LMA-SOFCs is that a direct electrochemical reaction is occurring between fuel (either hydrogen or coal) and oxygen transferred across the liquid Sn-Pb anode and the YSZ membrane. This finding allows, theoretically, for an increase in the maximum electric potential obtained from the fuel cell, from the metal oxidation potential to the full fuel oxidation reaction potential.
Chapter 3 References


Chapter 4

Electrochemical Impedance Spectroscopy of Liquid Tin Anode Solid Oxide Fuel Cell

The work presented in this chapter is an extension of a presentation given at the 219th Meeting of the Electrochemical Society, and published as in the Transactions of the Electrochemical Society as:


Preface to Chapter 4

In this chapter the final experimental work on the development of an LMA-SOFC experimental system and testing procedure are carried out. Equivalent circuits modeling of impedance spectra generated by the cell under argon, hydrogen, coal and coal-water slurry fuels are carried out. This collaborative project with the United States Department of Energy was focused on development of a reliable LMA-SOFC test system and evaluation protocol. This chapter focuses on a pure Sn anode LMA-SOFC and the equilibrium potential and impedance spectra of the system. Finally, the system is also used to generate power under hydrogen and to characterize the stability of the LMA material under high current density conditions.
Abstract

A liquid Sn anode solid oxide fuel cell is operated at 900 °C with a variety of fuel feeds, including argon, hydrogen, coal and a coal-water slurry. Characterization of anode performance is carried out by open circuit potential monitoring, linear potential sweeps, and electrochemical impedance spectroscopy combined with equivalent circuit modeling. A cathode symmetric cell is analyzed and modeled to isolate impedance contributions resulting from ionic resistance, cathode mass transport, and cathode charge transfer; results are used to isolate anode mass transport and charge transfer impedances in the fuel cell. Open circuit potential measurements under hydrogen fuel indicate that the dominant anode reaction is electrochemical oxidation of H\(_2\), while oxidation of Sn to SnO\(_2\) becomes the principal anodic process when the cell is fed with argon, coal, or coal-water slurry. Some chemical reduction of SnO\(_2\) to Sn by chemical reaction with coal is indicated by the cell potential.

Introduction

Solid oxide fuel cells (SOFC) technology is capable of generating electrical power from the oxidation of a variety of gaseous and liquid hydrocarbon fuels [1-3]. Typical anode designs for SOFCs fueled by liquid or solid fuel possess a porous cermet structure containing deposited catalytic material [4-5]. Porous anode designs have been used to oxidize a variety of hydrocarbons including gaseous, liquid and reformed solid fuels; however, significant performance degradation resulting from solid carbon
deposition (coking) results and solid carbonaceous fuel oxidation is infeasible in a porous anode SOFC [1-5].

Recent studies have been reported for SOFCs utilizing a novel liquid metal anode (LMA) design [6-21]. Pure liquid metals or liquid metal alloys are considered as potential anodes for the direct consumption of solid carbonaceous fuels in SOFCs [7-20]. Liquid metal anode solid oxide fuel cells (LMA-SOFC) are hypothesized to function by the following mechanism: the electrochemical reduction of $O_2$ from air to $O^{2-}$ ions occurs at the cathode; the oxygen ions are then conducted through a dense ceramic electrolyte membrane; the $O^{2-}$ ions then electrochemically oxidize the liquid metal anode to a metal oxide freeing two electrons that dissipate their potential in an external circuit before returning to the cathode for $O_2$ reduction; finally the addition of fuel to the LMA initiates a chemical reduction of metal oxide (regenerating the LMA) and chemical fuel oxidation (producing the fuel oxidation products) [9].

Studies have recently been conducted on a variety of metals and metal alloys to determine properties favorable to LMA-SOFC operation. In general, desirable LMA material should demonstrate the following properties: liquid phase at operational temperatures; possess a partially or fully soluble oxide phase; demonstrate oxidation potential less than the fuel oxidation potential; and facilitate a reversible metal oxidation reaction [7,9]. Metals that have been considered thus far are Sn, Pb, Sb, In, Bi and a variety of their alloys [7,10,17].
This study applies the technique of electrochemical impedance spectroscopy to a liquid tin anode SOFC (LTA-SOFC) operating under standard conditions of temperature and fuel composition. Electrochemical Impedance Spectroscopy is a powerful tool that can be used to analyze and improve the performance of a fuel cell. It is used to characterize cell limitations and separate different processes occurring on different time-scales. A significant amount of effort have been put to relate the different arcs observed in the impedance spectra (real vs. imaginary impedance plots) with the physical transfer and transport parameters. The low frequency arc is attributed to the mass transfer resistance [22,23] and diffusion effects in a solid oxide fuel cell. The high frequency and medium frequency arcs are related to the ohmic and charge transfer resistances respectively[27]. Despite the large number of studies available in the literature on the application of EIS to solid oxide fuel cells, there is no record of interpretation of impedance spectra of a LTA-SOFC which describes the key processes governing the dynamics of the system. In this article, EIS technique has been used to determine the main processes affecting the overall performance of the system.

Impedance measurements are used to probe the electrochemical performance of the cell and inform hypotheses concerning ionic transport and reaction mechanisms. The data can be used to engineer superior LTA alloys and interfaces, as well as provide fundamental information for engineering a complete LTA SOFC system.
Experimental

Liquid Metal Anode Solid Oxide Fuel Cell Design

A yttria-stabilized zirconia (YSZ, 6 mol % yttria) crucible with a 2.54 cm diameter base and 0.15 cm thickness was utilized as the ionically conductive (O\textsuperscript{2-}) membrane, provided by McDanel Advanced Ceramic Technologies. The exterior base of the YSZ crucible was painted with lanthanum strontium manganite (LSM) paste, which consists of La0.8Sr0.2MnO3 suspended in terpenol (Fuel Cell Materials, LSM20-I). The LSM cathode was then sintered onto the crucible by heating from room temperature to 1150 °C at a rate of 10 °C min\textsuperscript{-1}, maintained at temperature for 12 hours then cooled at the same rate. Two gold leads (current collector and voltage sensor) were attached to the LSM electrode with silver paste.

The crucible shown in Figure 4-1 was fitted onto a machined YSZ support tube using Aremco Ceramabond 885 zirconia-based sealant. The interior of the crucible, having a total volume of 12.9 cm\textsuperscript{3} was partially filled with solid tin shot (99.999 % Sigma Aldrich). An alumina-sheathed thermocouple and two rhenium wires used as a current collector and a voltage sensor were placed inside the YSZ tube and were submerged into the tin once it became molten during heat-up. An alumina feed tube was supported above the anode for injection of Ar, H\textsubscript{2}, coal, coal-water slurry, or additional anode material.
Electronic Control System

The LMA-SOFC described above was inserted into the top of a vertically oriented Barnstead Thermolyne tubular furnace. Hydrogen and argon flow rates as well as exhaust flow were controlled by an Arbin Instruments Fuel Cell Test Station. The hydrogen and argon flow rates used in these experiments were 50 cm$^3$ min$^{-1}$ under standard conditions. Coal-water slurry was injected at a rate of 160 μl min$^{-1}$ via a syringe pump. All electronic experiments were controlled by a Solartron Analytical 1470-E Potentiostat.
Impedance spectra were analyzed with a Solartron Analytical 1252-A frequency response analyzer.

**Experimental Test Procedure**

A vertically oriented crucible-style LMA-SOFC with a 14.7 g tin anode fueled by hydrogen (unhumidified) was heated from 25 to 900 °C at a rate of 10 °C min\(^{-1}\). An air environment was maintained at the cathode. The open circuit potential (OCP) of the cell was monitored for a period of 3 hours. During OCP monitoring, 6 impedance spectra were taken in 30 minute intervals. Spectra were collected by applying a 10 mV potential alternating about the experimentally determined OCP over a range of frequencies from 300 kHz to 50 mHz.

Following OCP impedance monitoring the LMA-SOFC was subjected to a series of linear potential sweeps in the galvanic (spontaneous power generation) regime. The sweeps were potential controlled from the OCP to 0.4 V and back, for a total of ten sweeps during a ten-hour period. During this period the current response to the potential control was monitored. Finally following the ten-cycle galvanic polarization a final OCP impedance spectrum was collected, according to method used for the fresh cell.

A second crucible-style LMA-SOFC with a 17.6 g tin anode was prepared in an identical fashion to the first and heated under hydrogen from 25 to 900 °C. A three-hour
series of OCP monitoring and impedance spectroscopy experiments identical to the first cell were carried out to determine performance repeatability.

Following the hydrogen test, the fuel flow was replaced with an inert (unhumidified) argon flow. The OCP and impedance behavior of the LMA-SOFC under inert argon were characterized by another three-hour monitoring test, identical to the hydrogen test.

Finally, the LMA-SOFC response to coal and coal-water slurry fuels were analyzed. While maintaining an inert argon anode flow, 0.801 g coal was injected directly onto the anode. The OCP and impedance behavior of the cell were monitored for three hours. Finally, coal-water slurry (90 mass % of water) was injected at a flow rate of 160 μl min⁻¹, during which a final series of 3 hour OCP and impedance spectroscopy evaluations were completed.

**Coal Properties**

The coal used for both direct and coal-water slurry injections was high volatility A-bituminous coal originally obtained from the Pittsburgh seam, Washington County, Pennsylvania. Proximate analysis results of the as-received coal sample indicate: 6.07 % moisture, 6.91 % ash, 36.05 % volatile matter, 50.97 % fixed carbon. Ultimate analysis results of the as-received coal sample indicate: 73.41 % carbon, 4.87 % hydrogen, 1.47 % nitrogen, 1.49 % sulfur and 5.80 % oxygen. The received sample was stored under argon
and possesses a particle size less than 60 mesh. The gross heating value (as received) was 30.578 MJ kg$^{-1}$. The coal water slurry (90 mass % of water) was prepared using deionized water.

**Cathode Symmetric Cell and Test Procedure**

A cathode symmetric cell was prepared to determine the impedance contributions from the membrane and cathode. The base of a YSZ crucible, identical to that used in the LMA-SOFC design, was cut from the full crucible. This base was painted with two LSM electrodes in an identical manner to the full LMA-SOFC. Each electrode was fitted with two gold leads adhered to the cell with silver paste to permit four electrode measurements.

The cathode symmetric cell was subjected to a series of electrochemical experiments in an air fed furnace at 900 °C. First, the symmetric cell OCP was monitored to ensure identical chemical activities at each electrode. Following this a series of impedance spectroscopy measurements were carried out over a frequency range of 300 kHz to 50 mHz. Spectra were obtained by applying a 10 mV alternating potential around three cell potentials: OCP, 200, and 400 mV.
Equivalent Circuit Modeling

Equivalent circuits of LMA-SOFC with argon and hydrogen anode feeds were modeled by two independent circuits represented in Figure 4-2.

**Figure 4-2.** Equivalent circuit models used in fitting LMA-SOFC: Cathode symmetric cell as well as argon, coal and coal-water slurry anode fed LMA-SOFC model (top); Equivalent circuit model used to fit hydrogen fueled LMA-SOFC (bottom). Description of elements of the circuit models is provided in the text.

The first circuit model, shown in Figure 4-2, was used in fitting symmetric cell data as well as to fit argon, coal and coal-water slurry anode feeds. In the equivalent circuit, R1 modeled the ionic resistance from the solid electrolyte, R2 models the charge transfer resistance, G (Gerischer element) models the coupled kinetic and diffusion processes [27], and CPE 2 fits the RC time constant of the R2 and G. The Gerischer element is described as the solution of the Fick’s equations with a sink term dependent on
the local kinetics [24] and modeling data with a Gerischer element indicates diffusion process involved with a chemical reaction. The second circuit model in Figure 4-2 was used to fit the behavior of the LMA-SOFC at open circuit conditions while fueled by hydrogen. In the equivalent circuit, R2 modeled the total charge transfer resistance, R3 in combination with G simulates the mass transfer process coupled with the chemical reaction, CPE 2 fitted the RC time constant of R2 and CPE3 fitted the time constant of R3 and G.

Results

Cathode Symmetric Cell

The cathode symmetric cell at 900 °C with both electrodes exposed to air, using a four-electrode measurement technique, exhibits a very small open circuit potential of 160 μV. The impedance spectra generated by this cell at OCP and under two applied potentials, 200 and 400 mV, are plotted in Nyquist form (real vs. imaginary impedances) in Figure 4-3.
Figure 4-3 Impedance spectra generated by cathode symmetric cell at 900 °C (both electrodes under air). A 10 mV alternating potential is applied about the OCP as well as a 200 and 400 mV polarization. The frequency ranges from 10 kHz to 50 mHz, with decreasing frequency from left to right.

Equivalent circuit modeling of the cathode symmetric cell impedance spectra allows for the quantification of individual contributions to overall LMA-SOFC impedances originating from membrane and cathodic contributions. The cathode symmetric cell equivalent circuit modeling results, for 5.1 cm² active area cell, produce an ohmic (ionic) area specific resistance (ASR) of 4.13 Ω cm², and a combined charge transfer ASR from both LSM electrodes is 5.87 Ω cm². Taking half of the combined charge transfer and mass transfer resistances from the cathode symmetry cell we isolate the impedance generated by the LTA-SOFC cathode to be 2.94 Ω cm².
Liquid Tin Anode Solid Oxide Fuel Cell Fuel Dependence

The LMA-SOFC open circuit potential is studied under a variety of anode feed conditions at 900 °C. The hydrogen fueled LMA-SOFC maintains an OCP of 1.117 V, while under inert argon the OCP observed is 0.841 V. The impedance spectra collected from the LMA-SOFC under each anode condition at the open circuit potential are shown in Figure 4-4.

Figure 4-4. Impedance spectra generated by liquid tin anode SOFC at 900 °C under argon and hydrogen anode feeds. Both impedance spectra are obtained about the OCP of the cell, 1.117 and 0.841 V for hydrogen and argon, respectively. A 10 mV alternating potential is applied at a range of frequencies 10 kHz to 50 mHz plotted (left) and high frequency close-up (right).

Equivalent circuit modeling results for LMA-SOFC fed with argon and hydrogen are plotted over their experimental results in Figure 4-5.
Figure 4-5. Impedance spectra and equivalent circuit modeling results for inert argon at OCP of 0.841 V (left) and hydrogen fueled at OCP of 1.117 V (right) LMA-SOFC at 900 °C, air fed cathode.

The open circuit potential generated by the LMA-SOFC following a powdered coal injection (under argon) increases to 0.885 V from the OCP generated under inert argon alone of 0.841 V. The OCP generated by the cell under a stream of coal water slurry (90 mass % of water) carried by argon is 0.852 V. The impedance spectra generated at each anode feed at open circuit potential are shown in Figure 4-6. Modeling results of the dry coal and coal water slurry ohmic resistance (R1) produce respective ASR of 2.95 and 3.21 Ω cm², and charge and mass transport ASR (R2) of 1.73 and 1.42 Ω cm². The contribution of the Gerischer impedance is not significant in this case and it is reasonable to state that charge transfer is governing the system dynamics. The model parameters are presented in Table 4-1 and comparing the symmetry cell data with the cell powered by hydrogen, it is observed that charge transfer is mainly added by the cathode only.
Figure 4-6. Impedance spectra generated by LMA-SOFC while under an inert argon anode feed as well as with a coal injection and coal-water slurry injection stream (both under argon).
Table 4-1. Equivalent circuit modeling resistance parameters used in fitting LMA-SOFC impedance spectra to individual reaction steps (ionic resistivity, charge and mass transfer). Values are reported in resistance modeled in a 5.1 cm² active area cell.

<table>
<thead>
<tr>
<th>Impedance Contribution</th>
<th>LMA-SOFC Fueled by Hydrogen</th>
<th>Cathode Symmetry Cell</th>
<th>LMA-SOFC under inert argon</th>
<th>LMA-SOFC Fueled by Dry-Coal</th>
<th>LMA-SOFC Fueled by Coal-Water Slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohmic Resistance (Ω)</td>
<td>0.85</td>
<td>0.81</td>
<td>0.55</td>
<td>0.58</td>
<td>0.63</td>
</tr>
<tr>
<td>Charge Transfer Resistance (Ω)</td>
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<td>1.15</td>
<td>0.35</td>
<td>0.34</td>
<td>0.28</td>
</tr>
<tr>
<td>Mass Transfer Resistance (Ω)</td>
<td>2.83</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
**Figure 4-7.** Cell potential vs. current density generated by fresh LMA-SOFC with 14.7 g tin anode. Hydrogen fueled anode, air fed cathode, 900 °C. Elevated potential at low current density only observed in hydrogen fueled cell.
Figure 4-8. Cell potential (left) and current response (right) generated by fresh LMA-SOFC with 14.7 g tin anode, fueled by hydrogen at 900 °C. Potential controlled sweep from OCP = 1.117 to 0.4 V at a rate of 24 mV min⁻¹.

Performance Degradation in Liquid Tin Anode Solid Oxide Fuel Cells

The LMA-SOFC with a 14.7 g tin anode at 900 °C fueled by hydrogen is examined in a series of linear potential sweeps from the OCP (1.117 V) to the galvanic potential of 0.4 V. The cell potential-current relationship from the initial linear potential sweep is plotted in Figure 4-7. The cell potential and current response to ten full cycles occurring over ten hours are shown in Figure 4-8.

Impedance spectra are taken from the LMA-SOFC fueled by hydrogen before and after the 10 hour deep cycle galvanic potential sweeps. The impedance spectroscopy response to the performance degradation is shown in Figure 4-9. A significant increase in
total impedance magnitude is observed with cell degradation resulting mostly from a two order of magnitude increase in charge and mass transport ASR.

**Figure 4-9.** Impedance spectra generated by LMA-SOFC before and after degradation caused by 10 cycle linear potential sweeps from OCP = 1.117 to 0.4 V.

**Discussion**

The evidence derived through impedance spectroscopy analysis and equivalent circuit modeling of both a LMA-SOFC and a cathode symmetric cell make possible the quantification of individual contributions to full cell impedance originating within the
ceramic membrane and arising from cathode mass transport and kinetic limitations. Kinetic and mass transport processes within the anode and at the anode interfaces are also examined in this study. This process can be utilized to model impedance contributions under a variety of fuel conditions and during galvanic power generation.

The values of individual impedance contributions can be isolated in LMA-SOFCs using equivalent circuit modeling of impedance spectra from the full cell and cathode symmetric cell. However, the cathodic impedance contributions from charge and mass transport of 2.94 Ω cm\(^2\) generated by the single 5.1 cm\(^2\) cathode dominate the impedance contributions of the anodic performance in the LMA-SOFC design. Further analysis would be improved by the implementation of high performance cathode materials and preparation to minimize cathodic impedance contributions and improve the quantification of anodic behavior.

The OCP of 0.841 V generated by the liquid tin anode SOFC under argon results from the oxidation of liquid tin to solid tin dioxide and is nearly equal to the theoretical standard potential of 0.877 V for this reaction at 900 ºC. Although this value indicates an oxidation of Sn the variation from standard potential may result from a mixed oxidation potential resulting from either the oxidation of Sn to a Sn oxide other than SnO\(^2\) or the oxidation of some contaminate present in the liquid Sn; this potential difference may also result from a small O\(_2\) leak into the anode chamber despite pressure testing and a positive gauge pressure.
The OCP generated by the hydrogen fueled LMA-SOFC increases to the hydrogen oxidation potential of 1.117 V. This observation indicates that a route for direct electrochemical oxidation of hydrogen is available, though perhaps subject to an absolute limitation in rate. This is corroborated by the results from impedance spectroscopy, in which a unique impedance spectrum is generated by the cell at OCP fueled by hydrogen compared to argon. The Gerischer-style impedance behavior at low frequencies results from the transport of an oxygen species through the thick tin layer to the hydrogen fuel at the liquid tin surface. This behavior is not observed under an inert atmosphere, as the only electrochemical reaction in the anode would be the oxidation of tin at the electrolyte/anode interface, requiring no mass transport through the tin layer. A plausible reaction mechanism step that may produce the observed OCP and impedance spectroscopy results under only a H₂ atmosphere in low current conditions would be the solubility of small amounts of H₂ into the liquid Sn; allowing for their direct electrochemical oxidation at the Sn-YSZ interface. Although this behavior is not seen in the coal fueled LTA-SOFC, future liquid anode compositions may facilitate the dissolution of solid hydrocarbons within the liquid anode enabling a significant voltage efficiency boost at low current densities.

The OCP generated by the LMA-SOFC fueled by dry coal shows a nominal increase in OCP from 0.841 to 0.885 V. This is not indicative of a direct electrochemical reaction with coal but a partial chemical reduction of tin dioxide in the liquid tin anode effectively increasing the activity ratio of liquid metal to metal oxide. The impedance spectra generated by the LMA-SOFC with an inert argon atmosphere was very similar to
that of the cell while fueled by dry coal, further indicating that in the case of coal fueled liquid tin anode SOFCs the electrochemical portion of the overall reaction mechanism is identical to the oxidation of Sn. The increase in OCP however does demonstrate that coal is functioning, at least partially, as a fuel in the overall chemical-electrochemical reaction.

The effects of injecting a coal-water slurry, 90 % water by mass, into the anode chamber of the LMA-SOFC are similar to the injection of dry coal. The OCP od the LMA-SOFC after the coal-water slurry injection was 0.852 V; this being greater than the OCP of the inert argon anode feed but less than the dry coal fueled LMA-SOFC. The slight increase in OCP above the inert case is believed to result from a reduction of tin dioxide to liquid tin. However, the presence of an excess of water in the anode chamber retarded the reduction of tin dioxide yielding an activity ratio of tin to tin dioxide greater than that of the inert argon fed anode at equilibrium but less than that of the dry coal fueled LMA-SOFC. The impedance spectra generated by the coal-water slurry fueled LMA-SOFC is similar to both the dry coal fueled cell as well as the inert argon fed anode cell. This observation indicates a similar electrochemical portion of the overall reaction mechanism in both coal fueled cases as well as the inert argon case.

The durability of a liquid tin anode SOFC is tested using a series of linear potential sweeps. The result of these sweeps shows a decreasing current response with each successive cycle (Figures 4-8 and 4-9). The current response to second cell potential sweep is slightly greater than that of the initial potential sweep; this is not believed to be
a trait indicative of the LMA-SOFC electrochemistry but an effect of the physical system. The cause of this degradation is believed to be solid tin dioxide deposition at the electrolyte/anode interface.

The equivalent circuit fitting of impedance spectra after current induced performance degradation show a several order of magnitude increase in ionic resistivity as well as anode charge and mass transfer; indicating a drastic decrease in the effective active area of the cell. This large increase in impedance magnitude corresponds with the decreased current response resulting from galvanic polarization, and supports the hypothesis that tin is irreversibly oxidized to a solid tin dioxide layer that acts as a physical, ionic and electronic barrier between the liquid tin and the YSZ membrane. The change in impedance spectra resulting from the current induced LMA-SOFC performance degradation under hydrogen fuel is similar to that observed under an inert anode atmosphere by Jayakumar et. al. [7]. During the linear potential sweep a sharp increase in the current response to potential change is seen below approximately 0.875 V. This is believed to be the result of the primary electrochemical reaction shifting from fuel oxidation to tin oxidation. The window for stable operation of a LMA-SOFC is thus between the tin oxidation and fuel oxidation potential, so as to prevent irreversible damage to the anode. Minimizing the electrode overpotential through proper anode geometry and material choice is crucial to maximizing the cell’s power density.
Conclusion

An LMA-SOFC test system is designed and demonstrated to characterize potential anode materials. Equivalent circuit modeling of impedance spectroscopy data generated by both the LMA-SOFC and a cathode symmetric cell are used to separate individual contributions to the cell impedance. Hydrogen fueled liquid tin anode SOFCs demonstrate unique impedance behavior and elevated OCP when compared to inert argon or coal fueled cells. Coal and coal-water slurry injections slightly increase the OCP but have a negligible effect on impedance spectra. Further anode materials to be analyzed should focus on understanding the oxygen mass transport through the liquid anode.

The equivalent circuit modeling of LMA-SOFC impedance spectra demonstrate that cathodic impedance contributions, 2.94 Ω cm\(^2\) as determined by cathode symmetric cell, dominate at open circuit conditions in the inert argon, dry-coal and coal water slurry fueled case. The hydrogen fueled LMA-SOFC at open circuit conditions demonstrates both an equilibrium potential of 1.117 V and a unique mass transport impedance contribution of 14.4 Ω cm\(^2\). These values indicate the thermodynamics of a direct electrochemical reaction between hydrogen and oxygen as well as a reaction mechanism unique to the hydrogen fueled LMA-SOFC case, speculated to be the result of dissolved hydrogen diffusion through the liquid tin anode.
Chapter 4 References


Summary

This dissertation details the contribution of the author to the development of liquid metal anode solid oxide fuel cells, specifically the implementation of equivalent circuit modeling of impedance spectra generated by LMA-SOFCs and cathode symmetric cells under a variety of anode fuels and inert feeds to further understand the reaction mechanisms.

Chapters 1 and 2 outline the progress and limitations of SOFCs fueled by alternative and reformed fuel sources and begin to implement equivalent circuit modeling of impedance spectra to understand the nature of SOFC inefficiencies. Chapter 3 demonstrates a preliminary study into the performance of a variety of liquid metals as the anode material and demonstrates power generation from the oxidation of coal in a LMA-SOFC.

Finally, Chapter 4 presents a controlled analysis of a liquid tin anode SOFC under inert argon, hydrogen, coal and coal-water slurry fuel conditions. This analysis focusing on equilibrium potential, impedance spectroscopy and performance degradation is coupled with an analysis of a cathode symmetric cell using impedance spectroscopy and equivalent circuit modeling. The resulting performance analysis is used to characterize the viability of liquid tin as an anode material.
Conclusion

This dissertation provides a basis for the analysis of liquid anode materials to catalyze the electrochemical oxidation of fuels, including coal, in solid oxide fuel cells. The physical system developed, experimental techniques applied and equivalent circuit modeling can and should be employed to analyze a variety of liquid anode materials. Quantification of individual impedance contributions can allow for the fine tuning of anode material properties by alloying or doping the liquid metal anode to better function in the electrochemical oxidation of solid hydrocarbon fuels.

The pure tin anode analyzed in these studies demonstrated some favorable properties toward solid hydrocarbon oxidation in SOFCs. However, significant degradation of performance occurs under the current densities necessary for practical application. This degradation results from the largely irreversible formation of a solid tin dioxide layer between the YSZ membrane and liquid anode. A continued study of liquid tin anodes should include the addition of an alloying metal or dopant that would facilitate the solubility of metal oxide in the tin and/or improve the kinetics of the metal oxide reactions.

With continued study LMA-SOFCs hold the potential to contribute to future electricity generation from a range of solid hydrocarbon fuels. This dissertation has both demonstrated power generation by LMA-SOFCs fueled by coal and characterized the impedance behavior of LMA-SOFCs under a variety of equilibrium conditions using equivalent circuit modeling.
Suggestions for Future Research

Liquid metal anode solid oxide fuel cell development has the potential to significantly increase the efficiency of electricity generation from solid hydrocarbon sources, including coal and bio-mass. Although significant development in system design will be required for LMA-SOFC implementation, the focus of near term research should be on the development and analysis of new molten anode materials.

There are several specific anode material properties that should be improved in order to create a more viable technology. The anode must be able to oxidize electrochemically and rapidly reduce chemically with the fuel source. The equilibrium potential, or Gibbs free energy of reaction, of the metal oxidation reaction should be near to but less than the fuel oxidation potential. Solubility of metal oxide in the liquid metal or a well-mixed liquid-liquid interface is required to ensure minimal mass transport resistances. The material’s ability to contact the maximum surface area of fuel will directly affect reaction rates. Finally, any ability of the molten material to conduct oxygen ions could further improve the efficiency of chemical to electrical energy conversion in LMA-SOFCs.
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Publications


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