COMPOSITE ARCHITECTURES FOR SUB-600 DEGREE CELSIUS FUEL CELLS

FEASIBILITY ANALYSIS AND FINAL EISG REPORT

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ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM

FEASIBILITY ANALYSIS REPORT (FAR)

COMPOSITE ARCHITECTURES FOR SUB-600° C FUEL CELLS

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PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to $62 million of which $2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University, which is under contract to the Commission.

The EISG Program conducts four solicitations a year and awards grants up to $75,000 for promising proof-of-concept energy research.

PIER funding efforts are focused on the following six RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

The EISG Program Administrator is required by contract to generate and deliver to the Commission a Feasibility Analysis Report (FAR) on all completed grant projects. The purpose of the FAR is to provide a concise summary and independent assessment of the grant project using the Stages and Gates methodology in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions (as presented in the Independent Assessment section).

The FAR is organized into the following sections:

- Executive Summary
- Stages and Gates Methodology
- Independent Assessment
- Appendices
    - Appendix A: Final Report (under separate cover)
    - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the FAR, please visit the EISG program page on the Commission's Web site at:
http://www.energy.ca.gov/research/innovations

or contact the EISG Program Administrator at (619) 594-1049 or email eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at http://www.energy.ca.gov/research/index.html.

Composite Architectures For Sub-600 ^{O}C Fuel Cells

EISG Grant # 99-35

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Introduction

Fuel cells incorporating a stack of solid oxide membranes can be highly efficient and environment-friendly systems for electrical power generation. Their broad implementation is, however, hindered by high capital costs and by performance issues that arise when low-cost configurations are contemplated. An essential characteristic of solid oxide fuel cell systems that can solve the cost problem is operation at temperatures much below the current operational domain of 850-1000^{0}C. Significant reduction in temperature creates the potential for the use of low-cost materials for metallic interconnects, fuel cell membrane support structures, and sealing. This EISG project targeted an important technical issue that limits the effective functioning of low-cost solid oxide fuel cells: offsetting the decreased electrode activity that accompanies reduction in temperature. This project addresses the PIER subject area of Environmentally Preferred Advanced Generation.

This EISG project studied the feasibility of configuring novel composite architectures for solid oxide fuel cells targeted for operation at or below 600^{0}C. It addressed the issue by formulating and characterizing composite electrodes functioning in laboratory cells between 550 and 700 ^{0}C.

The project led to the formulation of solid oxide fuel cell membrane assembly configurations and compositions, incorporating novel composite electrodes that can be expected to offer significant improvement over existing approaches.

Objectives

The goal of this project was to determine the feasibility of operating composite fuel cell membranes efficiently at 600^{0}C and below, while achieving an overall membrane area resistance of less than 1 Ω cm^{2} at these low temperatures. The following project objectives were established:

1. Develop a fuel cell membrane utilizing low cost colloidal techniques in the manufacture of the cell.
2. Develop a multilayer cathode supported fuel cell structure.
3. Measure cell performance, including membrane area resistance, at temperatures of 550 to 700ºC using both galvanostatic techniques and electrochemical impedance spectroscopy.
4. Develop a high performance multilayer cathode structure on an anode supported Yttria Stabilized Zirconia (YSZ) or Scandia Stabilized Zirconia (SSZ) electrolyte.
5. Develop a method for optimizing fuel cell electrodes at different temperatures.

Outcomes

1. The project formulated a novel solid oxide fuel cell membrane composite architecture.
2. The cathode supported membrane contained pinholes. It was estimated that insufficient time was available to develop a technique that would not result in pinholes on the membrane. As a consequence, anode supported fuel cell structure was introduced as objective 4.
3. The cathode consists of a dual layer of Lanthanum Strontium Manganate (LSM) compositions, with catalytic activity further enhanced by doping with cobalt.
4. Cathodes with various ratios of Lanthanum to Strontium were constructed and tested. Also, cathodes incorporating cobalt oxide were tested.
5. Cathode studies are particularly useful in optimizing fuel cell electrodes. The project used current versus over potential (Tafel) plots, and impedance spectra.
6. The investigator found that doping the cathode with cobalt could reduce cathode impedance at 600ºC, and increase the maximum power density by more than a factor of two; however, the goal of a 1 Ohm-cm^2 composite membrane resistance was not achieved at 600ºC.

Conclusions

1. The composite cathode structure developed is relatively easy to fabricate.
2. The membrane is best anode- rather than cathode- supported
3. The composite cathode structure consisted of a catalytic layer of LSM 85 / YSZ and a current collecting layer of LSM 45.
4. The best composite cathode structure consisted of a catalytic layer of LSM 85 / YSZ and a current collecting layer of LSM 45. Doping with Cobalt (not Cobalt Oxide) content was shown to improve performance at low temperatures.
5. Complete analysis of the kinetic data obtained from these experiments proved to be beyond the scope of this project. However, clear trends in performance, such as improvements due to Co doping, were readily apparent.

Benefits to California

Results of this research were presented at the San Francisco Local Section meeting of the Electrochemical Society. The research will also serve as a starting point for further research on cathode microstructure and kinetics at low temperature.

When the cathodes formulated as a result of this work are incorporated into commercial fuel cell structures, greater efficiency could be obtained at reduced temperatures. This can accelerate the adoption of solid oxide fuel cells for applications such as distributed power generation. This in turn would lead to reduced strain on the aging electricity transmission grid, greater reliability, and substantive cost savings due to greater efficiency.

Recommendations

The composite cathode architectures and materials identified in this project offer improved performance at lower temperatures. In particular, LSM 85 / YSZ catalytic layers exhibited the best performance at low temperatures. It is recommended that an anode-supported SOFC membrane configuration be adopted, with thinner composite cathodes than originally envisioned, and that the composite cathode be applied by the colloidal methods described in this work.

Stages and Gates Methodology

The California Energy Commission utilizes a stages and gates methodology for assessing a project's level of development and for making project management decisions. For research and development projects to be successful they need to address several key activities in a coordinated fashion as they progress through the various stages of development. The activities of the stages and gates process are typically tailored to fit a specific industry and in the case of PIER the activities were tailored to be appropriate for a publicly funded energy research and development program. In total there are seven types of activities that are tracked across eight stages of development as represented in the matrix below.

Development Stage/Activity Matrix

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8
Activity 1								
Activity 2								
Activity 3								
Activity 4								
Activity 5								
Activity 6								
Activity 7								

A description the PIER Stages and Gates approach may be found under "Active Award Document Resources" at: http://www.energy.ca.gov/research/innovations and are summarized here.

As the matrix implies, as a project progresses through the stages of development, the work activities associated with each stage needs to be advanced in a coordinated fashion. The EISG program primarily targets projects that seek to complete Stage 3 activities with the highest priority given to establishing technical feasibility. Shaded cells in the matrix above require no activity, assuming prior stage activity has been completed. The development stages and development activities are identified below.

Development Stages:	Development Activities:
Stage 1: Idea Generation & Work Statement Development	Activity 1: Marketing / Connection to Market
Stage 2: Technical and Market Analysis	Activity 2: Engineering / Technical
Stage 3: Research & Bench Scale Testing	Activity 3: Legal / Contractual
Stage 4: Technology Development and Field Experiments	Activity 4: Environmental, Safety, and Other Risk Assessments / Quality Plans
Stage 5: Product Development and Field Testing	Activity 5: Strategic Planning / PIER Fit - Critical Path Analysis
Stage 6: Demonstration and Full-Scale Testing	Activity 6: Production Readiness / Commercialization
Stage 7: Market Transformation	Activity 7: Public Benefits / Cost
Stage 8: Commercialization	

Independent Assessment

For the research under evaluation, the Program Administrator assessed the level of development for each activity tracked by the Stages and Gates methodology. This assessment is summarized in the Development Assessment Matrix below. Shaded bars are used to represent the assessed level of development for each activity as related to the development stages. Our assessment is based entirely on the information provided in the course of this project, and the final report. Hence it is only accurate to the extent that all current and past work related to the development activities are reported.

Development Assessment Matrix

Stages / Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Develop-ment	5 Product Develop-ment	6 Demon-stration	7 Market Transfor-mation	8 Commer-cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production. Readiness/								
Public Benefits/ Cost								

The Program Administrator's assessment was based on the following supporting details:

Marketing/Connection to the Market

No marketing activities were associated with this project beyond the presentation of results to the Electrochemical Society, San Francisco Local Section. Further technical risk reduction of the developed cathodes is recommended both at the cell level and at the stack level. Incorporation of the developed electrode configuration in commercial solid oxide fuel cell efforts may be anticipated.

Engineering/Technical

This EISG project constituted an important step in the development of low-cost, low temperature solid oxide fuel cells. The reduction in temperature of operation is enabled by the novel composite cathode architecture. Additional improvements in performance were obtained with the addition of cobalt by post-doping. A mechanism for testing new cathode materials and structures was described.

Legal/Contractual

The cathode fabrication process mainly involved known technology and as such, no intellectual property issues should arise. The cathode post-doping process may be covered under existing U.S. patents.

Environmental, Safety, Risk Assessments/ Quality Plans

The materials and techniques employed in the manufacture of the fuel cells with composite cathodes are not known to be especially hazardous. Where hazards exist, they can be handled in the approved manner as they were in the production of the prototype structures.

Quality Plans include Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety and Environmental**.**

Strategic

This product has no known critical dependencies on other projects under development by PIER or elsewhere

Production Readiness/Commercialization

The composite cathode structure developed is relatively easy to fabricate and could easily be incorporated into existing solid oxide fuel cell structures and those under development.

Public Benefits

Public benefits derived from PIER research and development are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system.
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the rate payer from this research is reduced environmental impacts of the California electricity supply or transmission or distribution system.

The technology developed can accelerate the deployment of low-cost solid oxide fuel cells that can serve in distributed power generation. The benefits include increased reliability of the electrical power supply and substantive cost savings through increased efficiency of the conversion of gas to electricity. Depending on the level of market penetration, the broad deployment of solid oxide fuel cells can save well over M$100/year for the California consumer

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)

Appendix A to FAR 99-35

ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM

EISG FINAL REPORT

COMPOSITE ARCHITECTURES FOR SUB-600°C FUEL CELLS

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Inquires related to this final report should be directed to the Awardee (see contact information on cover page) or the EISG Program Administrator at (619) 594-1049 or email eisgp@energy.state.ca.us.

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Abstract

The purpose of this project was the study of the feasibility of configuring novel composite electrodes for solid oxide fuel cells (SOFCs) that would enable effective operation at 600°C and below. This low temperature is in contrast to the 900-1000^{0}C operation of present-day solid oxide fuel cell systems. Achieving this objective greatly reduces materials compatibility problems, enhances solid oxide fuel cell lifetimes and reliability, and dramatically reduces their fabrication and operations costs.

A set of composite air electrode structures was produced and their electrical performance in laboratory fuel cells was determined. These composite positive electrode (cathode) structures were prepared using a glycine nitrate method for the production of their chief constituent: lanthanum-strontium-manganate (LSM). The electrodes included interlayers of LSM with different composition, as well as other oxides, to constitute the composite architecture. The electrodes were evaluated on yttria-stabilized zirconium oxide (YSZ) disk electrolytes as well as on thin electrolyte anode supported cells. This path of investigation was adopted because the resolution of thin-film processing issues together with the development and characterization of the novel cathode supported structures proved to be more than what could be accomplished in the contract period. The project thus allowed for the determination of the essential performance characteristics of the composites electrodes and the identification of the structure and composition of composite electrodes that can perform at the much-reduced operational temperature of the sub-600^{0}C solid oxide membrane fuel cells.

Key words:

Solid oxide fuel cell, composite cathodes, reduced temperature of operation

Executive Summary

Introduction

Fuel cells incorporating a stack of solid oxide membranes can be highly efficient and environment-friendly technologies for electrical energy generation. Their broad implementation is, however, hindered by high capital costs and by performance issues that arise when low-cost configurations are contemplated. An essential characteristic of solid oxide fuel cell systems that can solve the cost problem is operation at temperatures much below the current operational domain of 850-1000^{0}C. Significant reduction in temperature opens up the door to the use of low-cost materials for metallic interconnects, fuel cell membrane support structures, and sealing. The EISG project targeted an important technical issue that limits the effective functioning of low-cost solid oxide fuel cells: offsetting the decreased electrode activity that accompanies reduction in temperature. This project addresses the PIER subject area of Environmentally Preferred Advanced Generation.

The United States is the world's largest energy consumer and greenhouse gas generator, with an annual electricity use projected to be about 12.6 MWh (megawatt-hours) per person by 2015. While alternative energy sources are increasingly exploited, in the near and mid-term future a dominant fraction of electricity generation in California can be expected to be generated from a combination of fossil sources, chiefly coal and natural gas. In 1997, out of about 254×10^6 MWh of generation in California, more than 74×10^6 MWh were generated from gas. Electricity consumption is projected to continue to grow at a rate of approximately 2% per year.[1] Even a small percentage of improvement in the efficiency of generation amounts to an enormous dollar value, easily offsetting any development costs. At an average price of about 30$/MWh, a 5% increase in generation efficiency from gas alone would amount to a savings of over 100M$ per year for California. Solid oxide membrane fuel cells, operating at reduced temperatures, offer the possibility of achieving such savings.

This EISG project studied the feasibility of configuring novel composite architectures for solid oxide fuel cells targeted for operation at or below 600^{0}C. It addressed the issue by formulating and characterizing such composite electrodes when functioning in laboratory cells between 550 and 700 ^{0}C.

The project led to the formulation of solid oxide fuel cell membrane configurations and compositions, incorporating novel composite electrodes, that can be expected to offer significant improvement over existing approaches.

[1] http://www.energy.ca.gov/reports/2000-07-14_200-00-002.PDF

Objectives

The main objective of the work was the development and characterization of an efficient composite fuel cell membrane for operation at 600^0C and below, achieving an overall membrane area resistance of less than 1 Ω cm^2 at these low temperatures, by performing the following tasks:

Task1. Fabrication by means of colloidal methods of composite architecture SOFC membranes consisting of LSM support cathode (~2mm) optimized for electronic conductivity, porosity, and strength, together with a porous LSCM catalytic layer (5-20 μm), optimized for high surface exchange coefficient, incorporated in this electrode

Task 2. Integration of the electrode with a dense SSZ electrolyte layer

Task 3. Co-firing of the tri-layer composite membrane laminates

Task 4. Testing of the composite membranes (about 1" in diameter) in H_2-H_2O/air laboratory fuel cell rig, between 550 and 700^0C.

Task 5. Evaluation of cell performance and characteristics by I-V monitoring, and AC impedance spectroscopy.

Outcomes

1. The project formulated a novel solid oxide fuel cell membrane composite architecture
2. The membrane is best anode- rather than cathode- supported
3. The cathode consists of a dual layer of LSM compositions, with catalytic activity further enhanced by doping with cobalt.

Conclusions

A composite cathode architecture was developed for use in low temperature solid oxide fuel cells. The composite cathode structure consisted of a catalytic layer of LSM 85 / YSZ and a current collecting layer of LSM 45. These materials were chosen after trying other materials such as LSCM. A novel doping method was developed which was shown to improve performance with Co content at low temperatures. A cathode testing method was also implemented which will aid in the identification, development and understanding of cathode materials and structures at low temperatures.

Recommendations

The composite cathode architectures and materials identified in this project offer improved performance at lower temperatures. It is recommended that an anode-supported SOFC membrane configuration be adopted, with thinner composite cathodes than originally envisioned.

It is recommended to apply the composite cathode by the colloidal methods described in this work.

Public Benefits to California

Results of this research were presented at the San Francisco Local Section meeting of the Electrochemical Society. The research will also serve as a starting point for further research on cathode microstructure and kinetics at low temperature.

When the cathodes formulated as a result of this work are incorporated into commercial fuel cell structures, greater efficiency could be obtained at reduced temperatures. This can accelerate the adoption of solid oxide fuel cells for applications such as distributed power generation. This in turn would lead to reduced strain on the aging electricity transmission grid, greater reliability, and substantive cost savings due to greater efficiency.

Introduction

Background and Overview

The United States is the world's largest energy consumer and greenhouse gas generator, with an annual electricity use projected to be about 12.6 MWh (megawatt-hours) per person by 2015. While alternative energy sources are increasingly exploited, in the near and mid-term future a dominant fraction of electricity generation in California can be expected to be generated from a combination of fossil sources, chiefly coal and natural gas. In 1997, out of about 254×10^6 MWh of generation in California, more than 74×10^6 MWh were generated from gas. Even a small percentage of improvement in the efficiency of generation amounts to an enormous dollar value, easily offsetting any development costs. At an average price of about 30$/MWh, a 5% increase in generation efficiency from gas alone would amount to a savings of over 100M$ per year for California.

Since fuel use, such as natural gas, is inherently accomplished at elevated temperatures, efficient electrochemical technologies most likely involve fuel cells that operate above about 500ºC. Otherwise, costly and inefficient heat exchangers and reformers may be necessary to match fuel processing with fuel cell operating temperatures. The solid oxide membrane fuel cells offer the advantage of direct internal reforming of hydrocarbons, thereby eliminating the need for a separate fuel processor. They also deliver high quality heat that can be used for co-generation to reach overall efficiencies in excess of 80%. Efficiencies that are even higher can be predicted when multi-staged solid oxide fuel cell systems are considered, where the fuel cell itself has a sequence of temperature zones ranging from a 500-700^{0}C in the inlet zone to 950-1000 ^{0}C in the exit zone.[2]

A number of companies in the U.S. and abroad are developing a variety of solid oxide fuel cell systems. While impressive systems efficiencies and operating lifetimes have been demonstrated for systems operating around 1000^{0}C, there is a significant motivation for developing internally reforming SOFC modules that can operate in the range of 500-600^{0}C. Lowering of the fuel cell operating temperature vastly expands the range of compatible ancillary materials, such as interconnects and seals, and can allow deployment in applications where turbine co-generation might not be indicated, such as for residential environments. These are important advantages that can significantly reduce the cost of a SOFC system and widen the scope of the commercial market. There are, however, a number of technical issues that need to be resolved before the sub-600^{0}C SOFC is a viable complement to the higher temperature systems.

There are two major technical issues for the efficient functioning of the sub-600^{0}C SOFC: 1) use of an electrolyte with sufficiently low resistance to oxygen ion transport, and 2) the incorporation of a cathode of sufficient catalytic activity. In addition, the SOFC membranes must have adequate mechanical strength, and have an architecture that is stable on long-term use.

[2] "Next Generation Fuel Cells Workshop," November 3-4, 1998, *Workshop Proceedings*, December 1998.

Important also are economic factors. Installed SOFC costs have been a barrier to wide commercial acceptance, and therefore cost reduction of all system components must remain an objective in developing fuel cell systems and their expected manufacturing procedures.

The present proposal addressed these issues by developing and characterizing composite electrode architectures for efficient sub-600^{0}C fuel cells. The methods by which the composite membranes were produced involve colloidal processing and common ceramic processing techniques, thereby avoiding costly production steps.

Project Objectives

The overall project objective was the achievement of a membrane specific area resistance of less than 1 Ω cm^2 for a fuel cell operating at or near 600°C using moist hydrogen/air.
Specific EISG project objectives:

- Utilize low cost colloidal techniques in the manufacture of the cell.
- Develop a multilayer cathode supported fuel cell structure (Figure 1).
- Measure cell performance at temperatures of 550 to 700ºC using both galvanostatic techniques and electrochemical impedance spectroscopy.

Objectives modified during the project:

- Develop a high performance multilayer cathode structure on an anode supported YSZ or SSZ electrolyte.
- Develop a method for optimizing fuel cell electrodes at different temperatures.

The modified objectives are discussed in the Project Approach section.

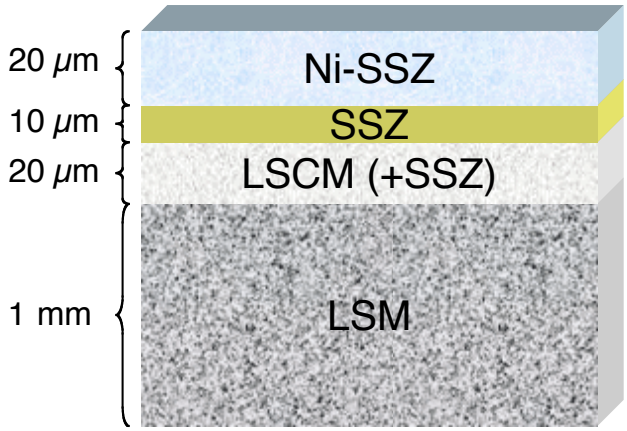


Figure 1. Fuel Cell Membrane With Proposed Composite Cathode Architecture

Project Approach

Project Work Plan

The original project was broken down into the following five tasks:

1) Fabrication by means of colloidal methods of composite architecture SOFC membranes consisting of LSM 45 support cathode optimized for electronic conductivity, porosity, and strength, together with a porous LSCM catalytic layer optimized for high surface exchange coefficient incorporated into this electrode.

2) Integration of the electrode with a thin film (5-10 μm) dense electrolyte layer by colloidal deposition.

3) Co-firing of the trilayer composite membrane laminates.

4) Testing of the composite membranes (about 1" in diameter) in H_2-H_2O/air laboratory fuel cell rig between 550 and 700ºC.

5) Evaluation of cell performance and characteristics by I-V monitoring and AC impedance spectroscopy.

Project approach modification

Developing the methods for obtaining a pinhole-free electrolyte membrane on the novel composite cathode supported structure was anticipated to exceed the time frame of the project , and the project objectives were accordingly modified. An anode-supported structure was found to be more practical than a cathode supported structure. In addition, to allow for an effective evaluation, a variety of composite cathodes examined in this project were tested on electrolyte disks rather than integrated with thin film structures. This change allowed greater flexibility in the testing of cathode materials with minimal impact on the overall project objective of a low specific area resistance at 600ºC.

Details of the cathode structure development and modifications are discussed in the Project Outcomes section.

Project Outcomes

Task 1 – Fabrication of composite cathodes

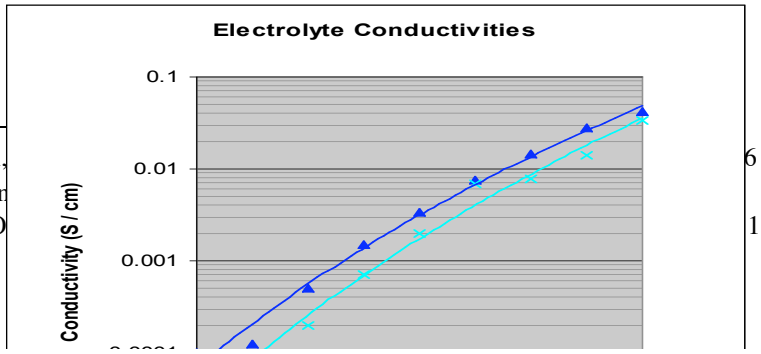
Many of the materials required for the proposed structure were not available commercially and had to be synthesized from chemical precursors. We chose to employ the glycine nitrate synthesis process (GNP) for the production of the LSM 45, LSM 85, LSCM and SSZ powders.[3] The first step in the GNP process consists of dissolving metal nitrates in the appropriate proportions with glycine in distilled water. The mixture is combusted on a hot plate to create a metal oxide ash. This ash is then calcined at 1200ºC for 2 hours in order to get the appropriate phase material. It is also often necessary to mill the powders for 2-3 hours to get the desired particle size.

As the materials synthesis and characterization was taking place, the cathode structure was developed using commercially available materials. LSM 65 was obtained from Praxair Specialty Ceramics. This composition was chosen for lack of reactivity with the YSZ electrolyte layer. The powder was mixed with binder and disks were pressed and pre-fired at 975ºC. An interlayer of LSM 65[4], YSZ and CoO was applied via colloidal spray. This preliminary cathode structure was characterized by SEM and checked for adequate sintering and porosity. A composite cathode structure was then made using the proposed materials (LSM 45, with an LSCM / SSZ interlayer).

Task 2 – Integration of electrode with electrolyte thin film

The SSZ electrolyte material fabricated using the GNP process first had to be characterized before being integrated into the fuel cell structure. An SSZ composition of 9 mol% scandia was identified as highly conductive and stable.[5] This material was pressed into disks and fired at 1500ºC to achieve greater than 90% theoretical density. Density was determined by volumetric analysis and SEM characterization. Platinum electrodes were fired onto the structure and conductivity testing was carried out at temperatures from 400 to 800ºC. Conductivity results appear in figure 2. As expected, the SSZ was more ionically conductive than the commercially available YSZ.

SSZ and YSZ films were deposited onto cathode supports using vacuum infiltration. Results appear in the following section.



[3] L. Chick, L. Pederson, 6 (1990).
[4] LSM 65= LSM x – lan
[5] Y. Arachi, H. Sakai, O 133-139 (1999).

Task 3 – Co-firing of tri-layer composite structure

SSZ and YSZ films were co-fired on composite cathode supports. Micrographs of the structures appear in figure 3. Both structures exhibit good adhesion between the film and cathode substrate. The first structure, made from the LSM 65, CoO, and YSZ, shows good porosity. The second structure made from the GNP LSM 45, LSCM / SSZ, and SSZ is too dense. However, neither structure was entirely free of pinholes.

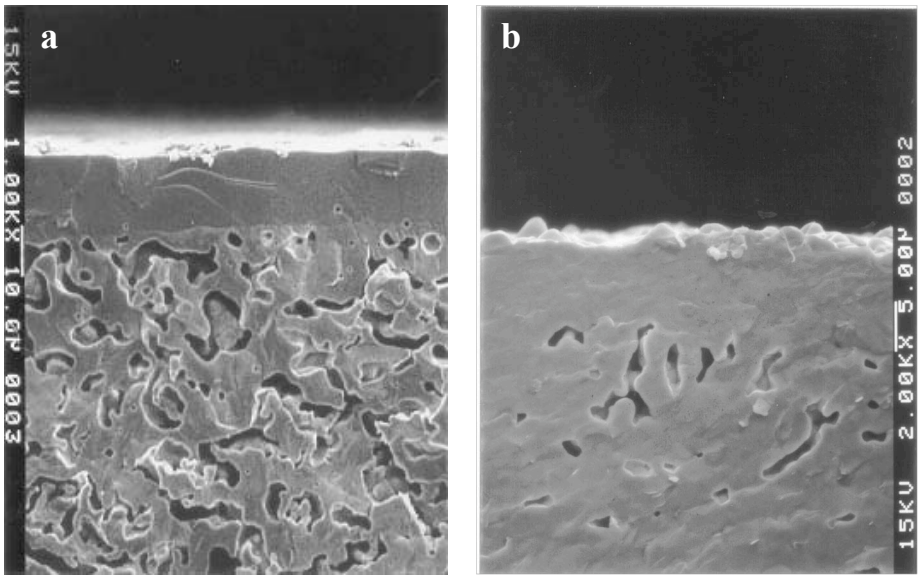


Figure 3. a) YSZ film on LSM 65 substrate with 10 micron LSM/CoO/YSZ interlayer b) SSZ film on LSM 45 substrate with LSCM/YSZ interlayer

Task 3 – modifications

Based on the limited performance characteristics of the cathode supported structures, anode supported structures were fabricated (see figure 4). A 50/50 wt% mix of NiO and YSZ was milled with binder and pressed into disks. The disks were pre-fired at 950ºC and a NiO / YSZ interlayer was applied via colloidal spray. The disks were then fired again and the electrolyte layer was applied by colloidal spray. The substrates and films were then co-fired at 1400ºC for 4 hours. Cathodes were then sprayed onto these structures from colloidal solution and fired at 1200ºC.

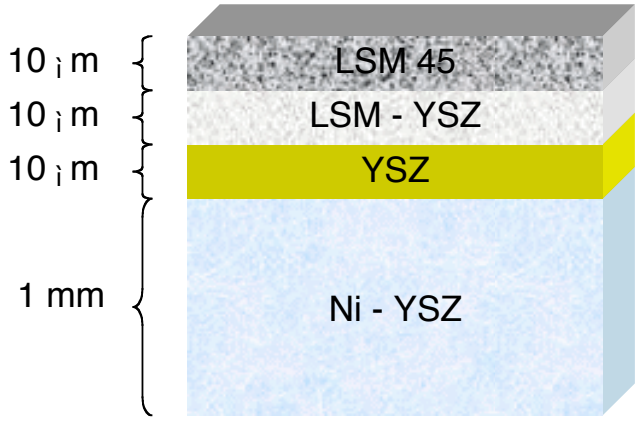


Figure 4. Anode supported structure schematic

Several anode supported cells were constructed. Minor modifications of the binder contents and substrate thickness were made to maximize performance at low temperature (substrates were made thinner and the pore former was eliminated). Micrographs of these structures appear in figure 5. Films of both YSZ and SSZ were used in these cells.

The anode supported structure allowed us to move to a more catalytic material for the interlayer—LSM 85. This occurred because the cathode on the anode supported structure was sintered at a much lower temperature than the original cathode in the cathode supported structure. The catalytic cathode interlayer consisted of a 50 / 50 wt% mix of the catalytic material and the electrolyte material. The catalytic interlayer was then covered by an LSM 45 current collect layer. These two layers made up the composite cathode on the anode supported cells.

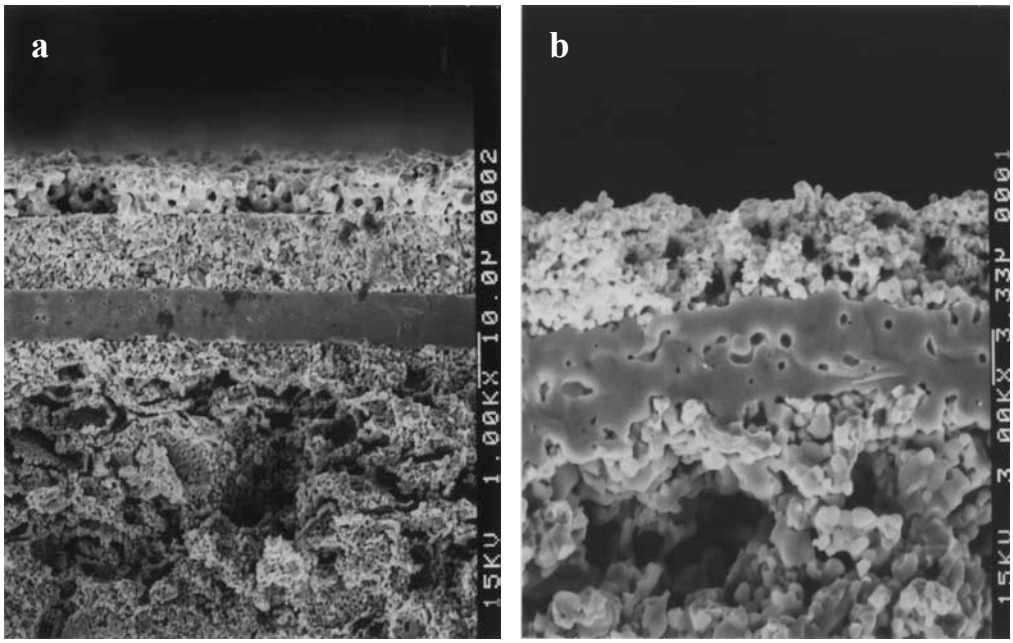


Figure 5. a) Anode supported YSZ film with LSM 85/YSZ catalytic interlayer b) Anode supported SSZ film with LSM 85/SSZ interlayer

Task 4 – Testing of composite membranes

Individual cells were mounted in a laboratory test rig for testing in moist hydrogen / air at temperatures from 500 to 800ºC. A schematic and picture of the test rig are shown in Figure 6. The schematic shows the typical cell geometry with the anode support in green. The composite cathode is applied to 1 cm^2 area and platinum screen is attached on both sides of the cell with platinum paste. The platinum screen is then spot welded to platinum wire for use in electrochemical measurements. The cell is sealed onto an alumina tube and moist hydrogen gas is circulated inside the sealed tube. A thermocouple is placed near the cell surface to monitor temperature.

Task 5 – Evaluation of cell performance

Cell performance was measured using galvanostatic and impedance techniques. The galvanostatic technique is the most common technique used to characterize fuel cell performance. Current is run through the cell and the cell voltage is monitored as a function of current. This gives data on device performance under real fuel cell operating conditions. Additionally, the power output of the cell can be determined by multiplying the current and the voltage at any particular point. Power density can be determined by this method and plotted versus current density. The maximum power density is a useful measure of the overall cell performance.

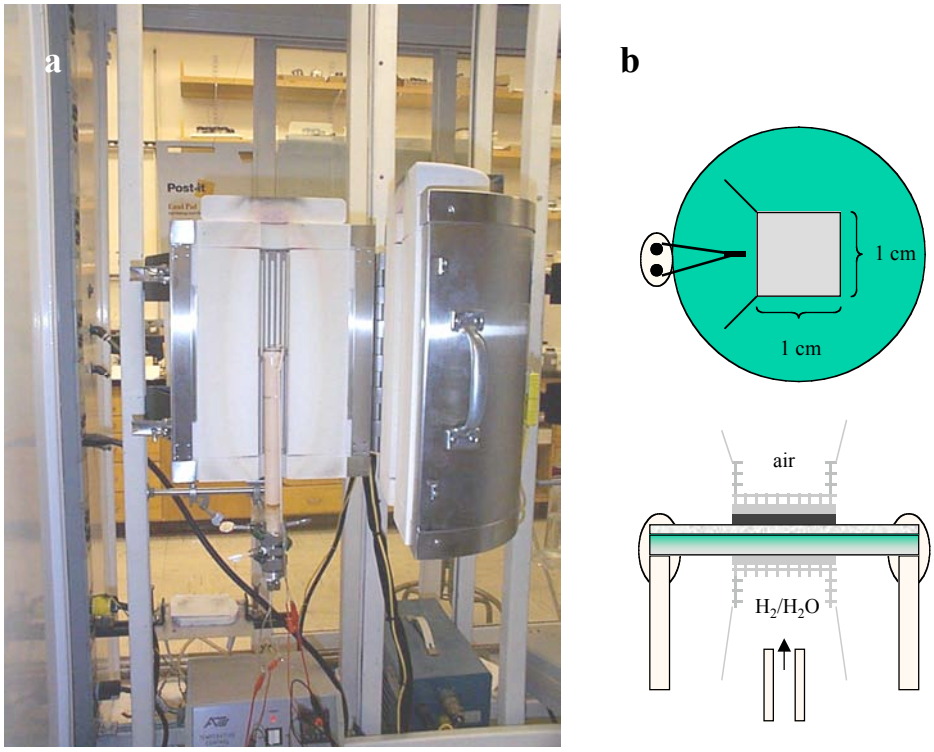
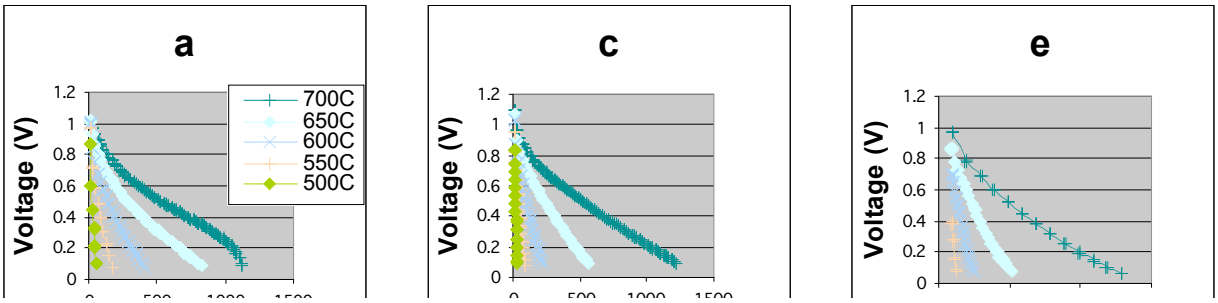


Figure 6. a) photograph of testing furnace and ceramic test rig
b) schematic of test cell geometry

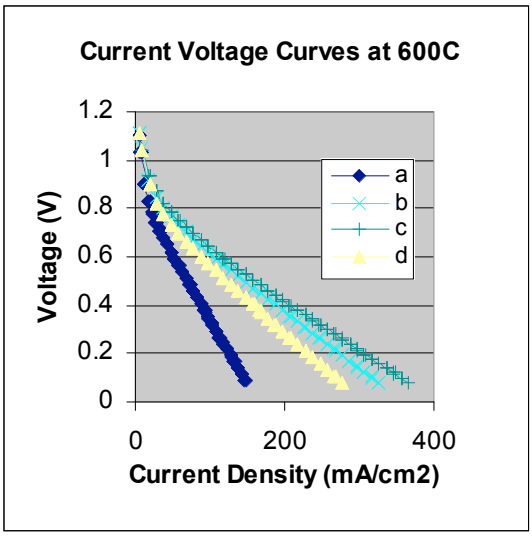
The other main electrochemical characterization technique utilized was electrochemical impedance spectroscopy. In this technique an alternating voltage perturbation is applied to the cell at various frequencies from MHz to mHz. The corresponding current response is measured. The components of the cell overpotential can be determined through appropriate analysis of the data so obtained.

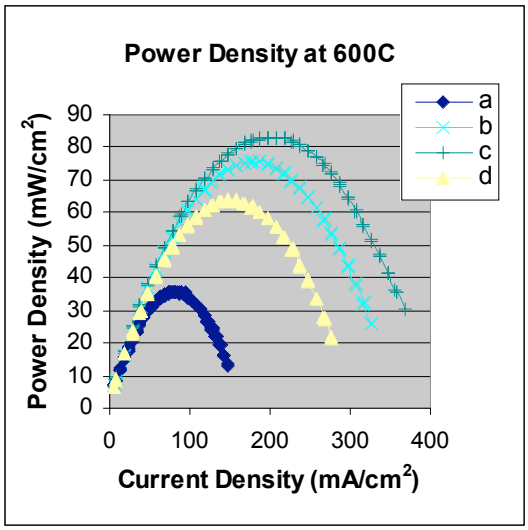
As a first step, we tested three cells using only galvanostatic techniques. The cells tested were produced on Ni / YSZ substrates similar to those shown in the micrographs in the previous section. All of the cells incorporated an LSM 45 layer in the cathode as a current collecting layer. The cells tested included: YSZ electrolyte with LSCM / YSZ catalytic layer, YSZ electrolyte with LSM 85 / YSZ catalytic layer, and SSZ electrolyte with SSZ / LSM 85 catalytic layer. Plots of the voltage versus current density and power density versus current density are shown in figure 6. From this figure we can see that at low temperatures, the cells with a YSZ electrolyte and an LSM 85 / YSZ catalytic layer have the best performance. The SSZ cell does not do as well because the electrolyte film does not appear completely sintered.



Once it was established that the cells with LSM 85 / YSZ catalytic layers exhibited the best performance at low temperatures, we decided to improve the performance through the addition of dopants. Cobalt and palladium had been observed to increase performance of cathodes in solid oxide fuel cells.[6, 7, 8] These materials were obtained in nitrate form and dissolved in distilled water. 8 μL of the solution (50 μg Co / cm^2) was then applied to the fuel cell cathodes and converted to the metal oxide in-situ during the cell test. The performance effects of these dopants were examined at temperatures from 550 to 700ºC (figure 8).

Current/voltage curves and current/power curves for the cells with LSM 85 / YSZ, LSM 45 composite cathodes appear below. Only the data taken at 600ºC is shown here. In the data plots "a" corresponds to the plain composite cathode after current conditioning, "b" to the cathode doped with Co after current conditioning, "c" to the cathode doped with larger amounts Co before current conditioning, and "d" to the cathode doped with larger amounts of Co after current conditioning. Pd doping was seen to decrease cell performance significantly at all temperatures and is not shown.





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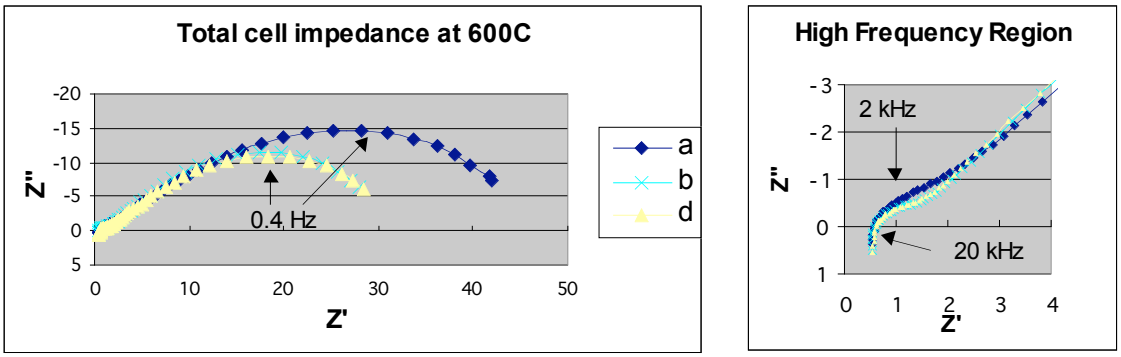

Figure 8. Effect of Co doping

At 600ºC we observed that cell performance improved dramatically with the addition of Co. Maximum power density went from 36 to 82 mW. The overall cell area specific resistance , which includes the anode, cathode, and electrolyte, was seen to decrease from 45 to 30 Ohm.cm^2 as a result of the introduction of Co by chemical infiltration of the cathode, as described above. Additional Co doping was seen to increase the cell performance slightly before current conditioning but not after current conditioning at 800ºC. The complex impedance appeared unchanged.

Task 5 – Expansion – cathode studies

The fuel cell cathode has been identified as the limiting factor in solid oxide fuel cell performance at most temperatures. This can be seen in figure 9. In the first plot showing overpotential contributions, the cathode is seen to dominate. The impedance spectrum confirms this as the cathode exhibits a very large resistance compared to the anode.

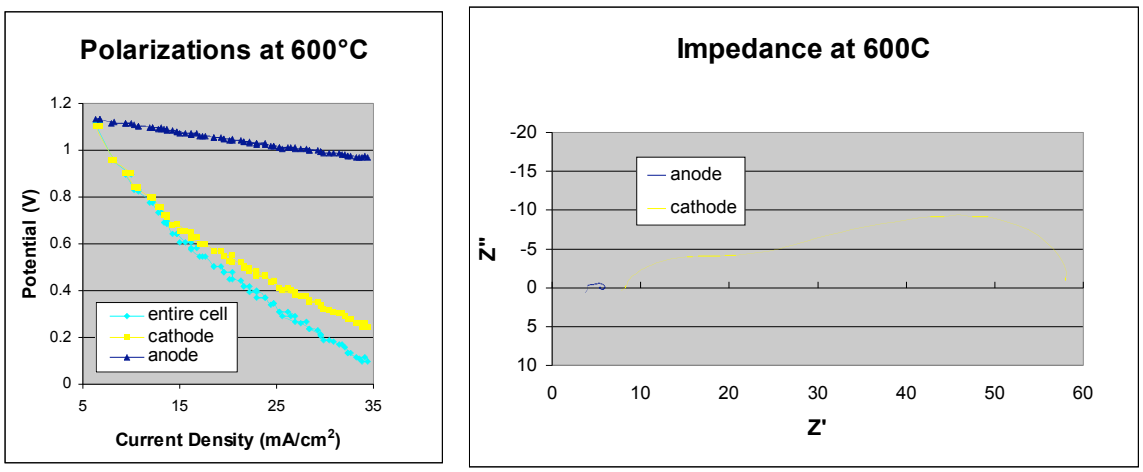

Figure 9. Contributions to total overpotential

The thin film geometry of the high performance fuel cell structure makes it difficult to isolate overpotential contributions from the individual electrodes. Therefore, we found it advantageous to deposit symmetric cathodes on thick YSZ disks in order to separate and evaluate cathode performance using reference electrodes. Different cathode materials were sprayed onto fully sintered YSZ disks and sintered at 1200°C. Platinum current collects were applied to the test cells and galvanostatic and impedance analysis was performed at temperatures from 500 to 800°C. Optimized cathodes were then applied to high performance thin film structures.

Thick YSZ cathode studies were done for cathodes with the LSM 85 / YSZ catalytic layers (with and without Co addition), LSM 45, and LSCM. Overpotential curves and impedance results for the LSM 85 / YSZ cathodes are shown in figures 10 and 11. As with the studies on fuel cell structures, we found that the LSM 85 /YSZ cathodes doped with Co performed the best at low temperatures (smaller overpotentials and lower resistances).

Cathode studies are particularly useful due to the insight they give into the cathode mechanism. From the current versus overpotential (Tafel) plots, it is possible to extrapolate an exchange current for the cell reaction. This exchange current is a measure of the catalytic performance of the catalytic material. Impedance plots can also yield this exchange current as well as resistances and capacitances associated with different steps in the electrode reaction. Knowledge of these reaction steps can help us in developing better cathode materials and structures at low temperatures. Unfortunately, interpretation of tafel plots and impedance spectra can be complicated by diffusion effects and cell inductances. Complete analysis of the kinetic data obtained from these experiments proved to be beyond the scope of this project. Clear trends in performance, such as improvements due to Co additions, were readily apparent however.

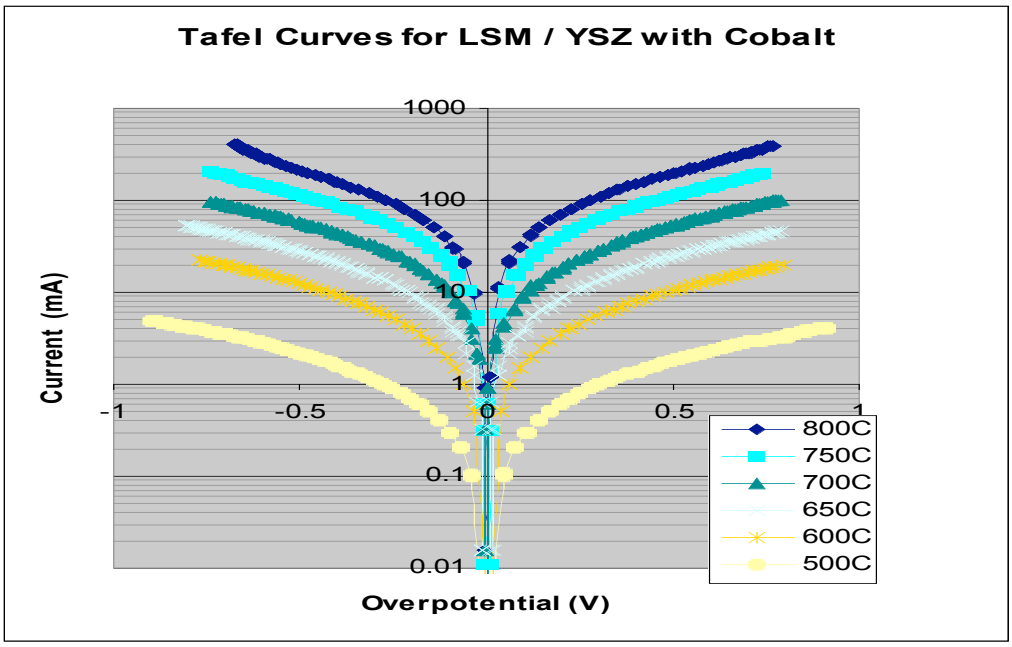

Figure 10. Overpotential curves for LSM 85 / YSZ cathodes with cobalt additives

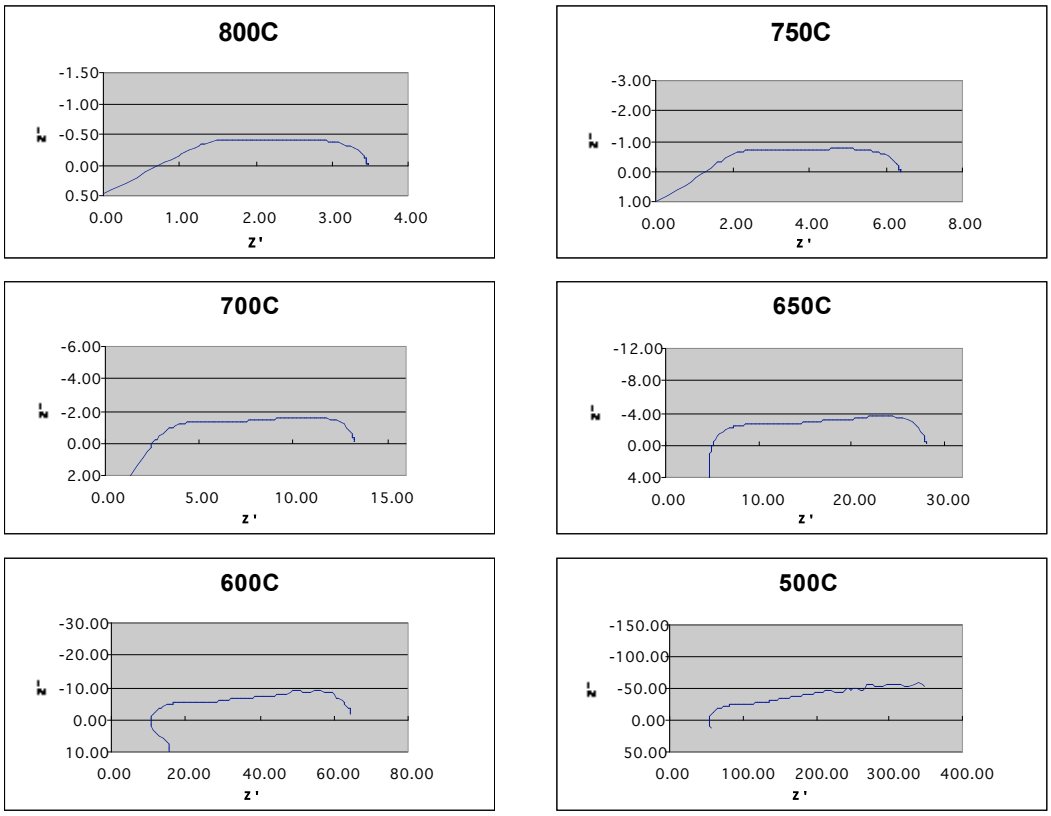

Figure 11. Complex impedance plots of LSM / YSZ cathodes with cobalt additive

Conclusions

A composite cathode architecture was developed for use in low temperature solid oxide fuel cells. The composite cathode structure consisted of a catalytic layer of LSM 85 / YSZ and a current collecting layer of LSM 45. These materials were chosen after trying other materials such as LSCM. A novel doping method was developed which was shown to improve performance with Co content at low temperatures. A cathode testing method was also implemented which will aid in the identification, development and understanding of cathode materials and structures at low temperatures.

Recommendations

The composite cathode architectures and materials identified in this project offer improved performance at lower temperatures. It is recommended that an anode-supported SOFC membrane configuration be adopted, with thinner composite cathodes than originally envisioned. It is recommended to apply the composite cathode by the colloidal methods described in this

work. The structure should be economical as low cost colloidal techniques were utilized to fabricate the structure.

Public Benefits to California

Results of this research were presented at the San Francisco Local Section meeting of the Electrochemical Society. The research will also serve as a starting point for further research on cathode microstructure and kinetics at low temperature.

When the cathodes formulated as a result of this work are incorporated into commercial fuel cell structures, greater efficiency could be obtained at reduced temperatures. This can accelerate the adoption of solid oxide fuel cells for applications such as distributed power generation. In turn, this in turn would lead to reduced strain on the electricity transmission grid, greater local reliability, and substantive cost savings due to greater efficiency.

Development Stage Assessment

Table 1. Development Assessment Matrix

Stages / Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Develop-ment	5 Product Develop-ment	6 Demon-stration	7 Market Transfor-mation	8 Commer-cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production. Readiness/								
Public Benefits/ Cost								

Marketing

No marketing activities were associated with this project. Further technical risk reduction of the developed cathodes is recommended both at the cell level and at the stack level. Incorporation of the developed electrode configuration in commercial solid oxide fuel cell efforts may be anticipated.

Engineering/Technical

This EISG project constituted an important step in the development of low-cost, low temperature solid oxide fuel cells. The reduction in temperature of operation is enabled by the novel composite cathode architecture. Additional improvements in performance were obtained with the addition of cobalt by post-doping. A mechanism for testing new cathode materials and structures was described.

Legal/Contractual

The cathode fabrication process mainly involved known technology and as such, no intellectual property issues should arise. The cathode post-doping process may be covered under existing U.S. patents.

Risk Assessment

The materials and techniques employed in the manufacture of the fuel cells with composite cathodes are not known to be especially hazardous. Where hazards exist, they can be handled in the approved manner as they were in the production of the prototype structures.

Strategic

The project has no known dependencies on other projects under development by PIER. The project addresses the PIER goals of advancing research in new energy generation technologies.

Production Readiness

The composite cathode structure developed is relatively easy to fabricate and could easily be incorporated into existing solid oxide fuel cell structures and those under development.

Benefit/Cost

The technology developed is of ultimate benefit to the California electricity consumer. It can accelerate the deployment of low-cost solid oxide fuel cells that can serve in distributed power generation. The benefits include increased reliability of the electrical power supply and substantive cost savings through increased efficiency of the conversion of gas to electricity. Depending on the level of market penetration, the broad deployment of solid oxide fuel cells can save well over M$100/year for the California consumer.

Glossary

AC	alternating current
CoO	cobalt oxide
I-V	current –voltage
LSCM	$La_{0.75}Sr_{0.2}Mn_{0.9}Co_{0.1}O_3$
LSM x	lanthanum strontium manganate (where x is $La_{0.x}Sr_{(1-0.x)}MnO_3$)
LSM 45	LSM x where x= 45
NiO	nickel oxide
SEM	scanning electron microscopy
SOFC	solid oxide fuel cell
SSZ	scandia stabilized zirconia $(Sc_2O_3)_{0.09}(ZrO_2)_{0.91}$
YSZ	yttria stabilized zirconia $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$

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