



CALIFORNIA
ENERGY
COMMISSION

ENERGY INNOVATIONS SMALL GRANT PROGRAM
Environmentally-Preferred Advanced Generation

**DIRECT OPERATION OF SOLID OXIDE
FUEL CELLS ON NATURAL GAS**

FEASIBILITY ANALYSIS

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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>.

Direct Operation of Solid Oxide Fuel Cells on Natural Gas

EISG Grant # 99-30

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Introduction

This research project targeted the generation of electricity using natural gas direct from the pipeline to operate fuel cells instead of processed gas. A combination of factors—low noise, high efficiency, ultra-low emissions, and the ability to utilize readily available natural gas—make fuel cells a generally desirable generation method.

Most fuel-cell systems consume hydrogen derived from natural gas using some form of fuel processor. The fuel processor adds considerable complication and expense to fuel-cell systems, exacerbating the problem of bringing costs down to competitive levels, especially for smaller plants. Until recently, it has not been thought possible to operate fuel cells directly on hydrocarbons. Recently, low-temperature, solid-oxide fuel cells (SOFC) have operated directly on methane. This demonstration signals an important new opportunity for making simple, cost-effective fuel cells. Fuel-cell operation on pipeline natural gas is considerably more difficult than operation on pure methane because pipeline gas contains higher hydrocarbons. This project developed a fundamentally new type of fuel-cell anode with a specific anode composition. This anode was successfully tested on propane, a higher hydrocarbon constituent of natural gas.

Objectives

The goal of this project was to determine the feasibility of anodic fuel conversion for a SOFC operating directly on natural gas. The key innovation was to develop the anode composition that satisfied the requirements for fuel-cell operation. Subsequently, the researcher verified that electrochemical oxidation of the higher hydrocarbons present in natural gas could take place without carbon deposition at the fuel-cell anode. The project set the following objectives:

1. Develop multiple SOFC anodes based on ceria with reduced Ni content and Ru-ceria. During the project a third composition using a conductive ceramic was added.
2. Eliminate carbon coking on the anode when the SOFC is operating on propane. Characterize each anode performance by scanning electron microscopy for detection of carbon on the anodes, impedance spectroscopy, and fuel-cell current-voltage measurements.
3. Verify anode performance in a fuel-cell stack. Select the most promising anode compositions for operation with natural gas. Incorporate the selected anodes into fuel cells and test as a function of fuel composition and temperature.

Outcomes

1. Ceria-based anodes with reduced Ni content, Ru-ceria anodes, and anodes using a conductive ceramic with greatly reduced Ni were constructed. Evaluation of these anodes found that they exhibit the required physical characteristics of porosity and conductivity. The conductive ceramic anode reduced the function of the metallic component to that of a pure catalyst. This

allowed the researcher to make a major reduction in the amount of noble metal in the catalyst.

2. The anodes were characterized. Impedance spectra proved acceptable. Coking on the anodes was evaluated. Results showed that Ru and Ni provide similar electrochemical performance. Less coking was found on the anodes with reduced metal fraction. However, at very low metal content, there is insufficient conductivity in the anode. From these data the research developed the innovation of replacing the metal with a conductive ceramic. This is a key outcome of this project. The innovative anode is composed of three materials: an electronically conducting ceramic, an ionically conducting ceramic, and a metallic catalyst. It is highly resistant to coking.
3. Gadolinium-doped-ceria (GDC) anodes with reduced Ni content (Ni-GDC) and the ceramic Ni anodes were chosen for fuel-cell testing. Initial performance using hydrogen fuel and air indicated only small differences between the two anode compositions. All subsequent testing focused on the ceramic Ni anodes. Performance using methane and air was similar to known performance of prior methane fuel cells. When operating on propane fuel and air, the ceramic Ni anode performed better than the Ni-GDC anodes. Further, after several hours of operation at peak power, the ceramic Ni anodes were free of coking, while the Ni-GDC anodes showed heavy carbon deposition (gram quantities).

Conclusions

1. This project has verified the feasibility of operating solid-oxide fuel cells (SOFC) directly on pipeline-quality natural gas. In California the gas is composed of methane and higher hydrocarbons, with controlled amounts of sulfur in the form of mercaptans, odiferous sulfur compounds deliberately added as required by law for safety purposes. Fuel fed to any operational fuel cell presumably would be free of mercaptans to avoid poisoning of the metallic catalyst. Removal techniques include use of activated carbon filters, zinc oxide, or zinc acetate.
2. This project tested SOFC performance on higher-hydrocarbon components of natural gas, and it showed that the fuel cells can be operated with propane.
3. After testing Ni-ceria and Ru-ceria anodes, the researcher determined that anodes with very low Ni content perform well with a ceramic conductor to provide anode conductivity. That is, they provide fast electrochemical oxidation, and hence high power densities, without carbon deposition.
4. This researcher utilized two ceramic constituents with an embedded metallic catalyst in his design approach. Because the relative amounts and the chemical nature of each of the three constituents can be altered to match a specific fuel or operating condition, a designer has great flexibility for improving fuel-cell performance.
5. A major advantage of the new anodes is that they can be cyclically reduced and oxidized without degrading performance. This redox cycling is expected to occur regularly during periodic shutdown of small generators when the fuel flow is stopped. Thus, the new SOFC anodes may enable new applications of SOFCs that rely on the direct use of high-energy-density hydrocarbon fuels or feature frequent on-off cycling (e.g. portable power, auxiliary power units, and distributed generation.) While early stability tests of these anodes are promising, longer-term tests are needed.

Benefits to California

The PA's assessment is that the benefits to be derived by the California electric ratepayer from the continuation and successful conclusion of this line of research accrue in the area of

distributed generation. Distributed generation benefits directly from the availability of a quiet, low-emission, cost-effective power source using a readily available fuel. By operating on both natural gas and propane, these fuel cells can be configured as uninterrupted power sources for the communities they serve. At an estimated thermal efficiency of from 40% to 60%, these fuel cells reduce the amount of carbon dioxide produced per unit of electricity, thereby reducing the detrimental effect from this assumed greenhouse gas. Production of high-grade heat ($\sim 700^{\circ}\text{C}$) as a byproduct can substantially improve the overall fuel efficiency of the distributed-generation network by situating the generator facilities as combined heat and power installations. Such a configuration is feasible given the quiet, non-polluting nature of fuel cells.

Recommendations

In order to advance this technology towards commercialization, R&D efforts must be carried out to improve and optimize the structure and composition of the new ceramic anodes for use with natural gas. This research should investigate and determine the following:

- The effects of sulfur-containing compounds should be assessed in order to determine whether the SOFC generators using these new anodes will require the removal of sulfur from the fuel. If filtering of the gas is required, toxicity of used filters and their proper disposal require evaluation.
- The long-term behavior of SOFC fuel cells incorporating these anodes must be assessed.
- Development criteria should require that the anodes achieve stable long-term performance.
- The long-term test should include frequent cycling of operating conditions, including exposure to air, as expected in the real operation of small SOFC generators.
- Finally, the anodes should be used as the support element of thin-electrolyte SOFCs. This matches the SOFC configuration being commercially developed and will provide the best overall performance.

This research effort should be undertaken in tandem with a commercializing partner. If these anodes can be incorporated into the existing SOFC configuration of commercial interest, it will maximize the prospects for this new technology.

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	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

This research discovered a new method of composing SOFC anodes. As such, it has been premature to consider the market until now. Very little has been done beyond recognizing the proper mechanical design to enable the retrofitting of the new anode into the existing designs of fuel cells under development. A commercializer has yet to be chosen.

Engineering/Technical

This project was limited to a feasibility study, but it discovered a heretofore unrealized method of SOFC anode composition. It will take additional testing to understand and optimize the operating parameters for the method and for other fuels.

Legal/Contractual

Northwestern University, the Principal Investigator, and the research team have registered a patent disclosure for this innovation. The California Energy Commission may hold certain rights.

Environmental, Safety, Risk Assessments/ Quality Plans

Quality planning must be done prior to completion of stage 4 development. Quality Plans include Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety and Environmental Plans.

Strategic

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

Production Readiness/Commercialization

Significant research and development remains before production can occur, but recognition that the new anode may be a retrofit item in existing designs means that fuel cells incorporating this new technology could enter the marketplace very quickly.

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 technology developed in this project advances fuel-cell development in general, which is considered a key technology for distributed generation. The use of fuel cells in distributed generation offers the following potential benefits to California electric ratepayers: (a) reduces harmful environmental emissions that result from central power plants using combustion technologies, (b) reduces the need for power-distribution infrastructure, (c) increases grid reliability, (d) increases the quality of the power grid and eliminates power-line losses.

In addition to the general benefits derived from distributed generation, the specific technology developed in this project has the potential to reduce the capital and operating costs of Solid Oxide Fuel Cells. The inventor has made significant progress in designing a fuel cell to run directly on natural gas. That eliminates the need for an expensive and complex reformer, and it allows the fuel cell to be connected directly to existing natural gas lines to serve as the fuel source. SOFCs also can be configured to generate hot water or heat, further increasing their energy efficiency.

Fuel cells generally have high thermal efficiency. When compared to conventional electric generators, this means that a higher percentage of the fuel is converted to electricity. Less fuel is consumed and less carbon dioxide gas is produced. The reduced greenhouse emissions and the lower consumption of expensive imported fuel are benefits which extend beyond the electric ratepayer to the population in general.

Program Administrator Assessment

After taking into consideration: (a) research findings in the grant project, (b) overall development status as determined by stages and gates and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for follow-on funding within the PIER program.

Receiving follow-on funding ultimately depends upon: (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation and (c) successful evaluation of the proposal.

Appendix A: Final Report (under separate cover)

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

Appendix A to FAR 99-30

**ENERGY INNOVATIONS SMALL GRANT
(EISG) PROGRAM**

EISG FINAL REPORT

**DIRECT OPERATION OF
SOLID OXIDE FUEL CELLS ON NATURAL GAS**

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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

Fuel cell electrical generators can use readily available natural gas, but only via the use of fuel processors that reform the hydrocarbons to hydrogen that most fuel cells can use. The fuel processor adds considerable complication and expense to fuel cell generators, exacerbating the problem of bring costs down to competitive levels, especially for smaller-scale plants. Until recently, it has not been thought possible to operate fuel cells directly on hydrocarbons. The recent demonstration of low-temperature solid-oxide fuel cell (SOFC) operation directly on methane signaled an important new opportunity for making simple, cost-effective power plants. The main aim of the proposed project was to demonstrate the feasibility of operating SOFCs directly on natural gas, which had not previously been demonstrated. The key problems were to verify that the higher hydrocarbons present in natural gas can be electrochemically oxidized and without carbon deposition at the fuel cell anode. For this, it was necessary to explore alternate SOFC anode compositions. Anode performance was characterized by chemical detection of carbon on the anodes, impedance spectroscopy, and fuel-cell current-voltage measurements.

This project showed the feasibility of natural-gas-fueled SOFCs. The higher hydrocarbons present in natural gas did cause coking problems with Ni-Ceria anodes. The originally proposed Ru-based composition did not provide good fuel cell performance, so it was not studied further. However, we identified a new anode composition, a composite of Ceria and LaCrO_3 with a small amount of Ni added, that provided good performance. SOFCs with the new anodes yielded good performance with both natural gas and propane fuels.

Executive Summary

1. Introduction

This research project targeted the clean generation of electricity using natural-gas fuel cells. A combination of factors - low noise, low emissions, compact size, and ability to utilize readily-available natural gas – make fuel cells a generally desirable generation method and allows fuel cell generators to be sited practically anywhere. However, key technical and cost barriers must be overcome prior to commercialization.

Fuel cell generators can use natural gas via fuel processors that reform the hydrocarbons to hydrogen that most fuel cells can use. However, the fuel processor adds considerable complication and expense to fuel cell generators, exacerbating the problem of bringing costs down to competitive levels, especially for smaller-scale plants. Until recently, it has not been thought possible to operate fuel cells directly on hydrocarbons. The recent demonstration of low-temperature solid-oxide fuel cell (SOFC) operation directly on methane signals an important new opportunity for making simple, cost-effective power plants. Nonetheless, cell operation on pipeline natural gas, which also contains higher hydrocarbons, is considerably more difficult than pure methane.

2. Project Objectives

In the proposed project, the feasibility of operating SOFCs directly on natural gas was tested. The key problems were to verify that the higher hydrocarbons present in natural gas can be electrochemically oxidized and without carbon deposition at the fuel cell anode. For this, it was necessary to explore alternate SOFC anode compositions. Anode performance was

characterized by chemical detection of carbon on the anodes, impedance spectroscopy, and fuel-cell current-voltage measurements.

3. Project Outcomes

This project showed the feasibility of natural-gas-fueled SOFCs. The higher hydrocarbons present in natural gas did cause coking problems with Ni-Ceria anodes. The originally proposed Ru-based composition did not provide good fuel cell performance, so it was not studied further. However, we identified a new anode composition, a composite of Ceria and LaCrO_3 with a small amount of Ni added, that provided good performance. SOFCs with the new anodes yielded good performance with both natural gas and propane fuels.

4. Conclusions

These results clearly indicate that it is possible to stably operate SOFCs with novel anodes on natural gas, and potentially on other practical fuels such as propane. However, the bulk-electrolyte cell used in this study in order to facilitate quick feedback on anode development, are not practical because they have limited power densities. Power densities of $\approx 0.5 \text{ W/cm}^2$ are expected to be competitive with other fuel cells, whereas the present cells produced $\approx 0.15 \text{ W/cm}^2$.

5. Recommendations

A critical next step in the development of these anodes is to incorporate them into thin-electrolyte SOFCs. This is required for practical devices in order to eliminate the substantial losses in thick-electrolyte SOFCs. Thus, it is suggested that the new anodes should be used in anode-supported SOFCs. In this case, the thin electrolyte is supported on a bulk anode, providing an optimal geometry to minimize ohmic losses in both the anode and the electrolyte. Furthermore, this is rapidly becoming an industry standard configuration, and the ability to use

this configuration will facilitate the incorporation of these new anodes into the schemes of a number of key SOFC developers.

6. Public Benefits to California

SOFC electrical generators will provide an alternative to building expensive new large-scale power plants and expanding transmission capacity, leading to savings to rate payers. Furthermore, the smaller fuel-cell generators can be added with relatively short lead time, providing a highly flexible and cost-effective method for responding to increased electricity demand. The fuel-cell generators can be connected into the grid, and the resulting distributed network would provide considerable flexibility in meeting demand and avoiding large-scale power outages. An additional benefit of localized generation is that the high-grade waste heat produced can be used on site, further increasing overall efficiency. Improved efficiency has important ramifications for reducing the greenhouse effect since less CO₂ is produced for a given amount of energy produced. Along these same lines, the operation on CH₄ fuel also minimizes CO₂ production.

Introduction

It is expected that demand for electricity will continue to increase in California and other areas of the US. In addition, it will be necessary to add new lower-pollution power plants to replace older plants. New large-scale power plants are a useful option in many cases, but they have very large capital costs. Also, because of their large size and long construction times, they must account for expected future increases in demand. New large-scale plants will also require expansion of transmission capacity. Another approach is to distribute a number of smaller power plants. The smaller plants can be brought up to speed more quickly, and provide a much more flexible response to changes in demand. However, smaller scale turbine-based plants are much less efficient than large-scale power plants. Furthermore, the siting of distributed turbine-based plants may be problematic because of the associated emissions and noise. A more efficient, unobtrusive power generation method is needed for effectively implementing distributed generation.

One potential solution to this need is the fuel cell. Fuel cells generally provide the lowest emissions of any non-renewable power generation method, and can yield extremely high energy efficiency even for small size plants. These factors, combined with the low noise and ability to utilize readily-available natural gas, allow fuel cell generators to be sited practically anywhere. The availability of such generators would yield savings to rate payers, compared to the alternative of building large-scale power plants and enhancing transmission networks. The fuel-cell generators would be connected into the grid, and the resulting distributed network would provide considerable flexibility in meeting demand and avoiding large-scale power outages. An additional advantage of localized generation is that the high-grade waste heat produced can be used on site, further increasing overall efficiency. Improved efficiency has important

ramifications for reducing the greenhouse effect since less CO₂ is produced for a given amount of energy produced. Along these same lines, the operation on CH₄ fuel also minimizes CO₂ production compared to higher hydrocarbons. The advantages of distributed generation and fuel cells have been well cited in the past (see EPRI report TR-100686 “Carbonate Fuel Cells as Distributed Generation Resources” (1992), EPRI report BR-101254 “Distributed Generation: Meeting the Urban Challenge” (1992), and the America Public Power Association “Notice of Market Opportunity” (1988).

A disadvantage of fuel cells has been that they generally operate only on hydrogen, which is currently neither readily available nor easily stored. Until recently, it has not been thought possible to operate fuel cells directly on hydrocarbons. Rather, fuel cell power plants employ fuel “reformers,” which convert fuels into hydrogen that the fuel cell can use. While reformers are useful for large-scale power plants (e.g. > 1 MW), the additional cost and complication is prohibitive for smaller scale plants.

We recently demonstrated that novel low-temperature ($\approx 600^{\circ}\text{C}$) solid-oxide fuel cells (SOFCs) can operate by direct oxidation of methane, without carbon deposition.¹ Remarkably, power densities with methane are quite high, e.g. 0.37 W/cm^2 at 650°C , only $\approx 20\%$ less than for the same cells operated on hydrogen. These results are unique since prior SOFC studies with dry methane, typically at temperatures $>800^{\circ}\text{C}$, showed that reforming and carbon deposition reactions dominated, and power densities were low. Carbon deposition was apparently suppressed at lower SOFC operating temperatures. However, attempts to operate with higher hydrocarbons, e.g. ethane and propane, showed that these fuels more readily produced carbon deposition. Natural gas, the likely fuel source for distributed fuel cell generators, contains not only methane but several percent of higher hydrocarbons and small amounts of sulfur

compounds. Thus, further work is required to determine if these novel fuel cells can be used for **Environmentally Preferred Advanced Generation** using natural gas.

This project has demonstrated the feasibility of a new type of anode that allows successful SOFC operation on natural gas. However, there are a number of steps required for this technology to reach the market. In particular, more R&D work is required to improve upon the initially developed composition. Then it would be important to incorporate the anodes into the new low-T SOFC configurations that are currently being developed by a number of major corporations, such that they can utilize this new technology. We believe that the novel anodes developed in this program can be incorporated into these cells, providing a rapid path to commercialization of this technology. A considerable amount of long-term testing would then be required to ensure stable operation. At this point, a serious commercialization effort would be merited.

Project Objectives

Project objectives were to:

- Verify the feasibility of operating solid-oxide fuel cells (SOFCs) directly on natural gas
- Determine conditions where carbon deposits on the fuel cell anode were determined using de-sulfurized natural gas.
- Test SOFC performance on higher-hydrocarbon components of natural gas.
- Determine the anode composition most appropriate for use with natural gas, with the candidates being Ceria-based anodes with reduced Ni content, and Ru-Ceria anodes.
- Characterize anode reactions using scanning electron microscopy to detect carbon deposition, impedance spectroscopy with an electrochemical interface, and SOFC current-voltage measurements.
- Develop anode compositions and structures that provide fast electrochemical oxidation, and hence high power densities, without carbon deposition.

Project Approach

The aim of the proposed project was to prepare and characterize SOFC anodes expected to be effective for oxidizing natural gas without carbon deposition, and to test their performance. Correlations of anode composition and structure with the rates of C deposition and electrochemical oxidation were made, and the results used to help understand reaction mechanisms. The tests were carried out with a typical natural gas (note that natural gases vary in composition), as well as methane and propane. The fuels were typically humidified with 3% water.

A. Anode Material Synthesis and SOFC Fabrication

The anodes were cermets containing the metals Ni and Ru combined with Gd-doped Ceria (GDC). Ceria, Ni, and Ru are chosen for their well-known activities for hydrocarbon oxidation. The anodes were deposited from slurries using colloidal deposition, sintering, and reduction in wet hydrogen. Electrochemically active layer thicknesses were typically 10 – 50 μm . In order to provide sufficient current carrying capability, a standard Ag or Pt ink current collector was deposited on top of the anode active layer.

The anodes were tested in SOFCs with bulk (0.5 mm thick) GDC electrolytes. Bulk electrolyte cells are a simple expedient for rapidly screening new anode materials, but even with the relatively high ionic conductivity of GDC, there is a substantial electrolyte ohmic loss at low temperatures. Dense 15-mm-diameter pellets were produced by pressing GDC powder (NexTech) and sintering at 1500°C for 6 hrs.

Commercial NiO and RuO₂ powders were used with the GDC powder to prepare the anodes. Anodes were prepared by weighing and mixing the powders, mixing with water and

polyvinyl alcohol, grinding, and then painting on one side of the GDC electrolyte pellet. Anodes containing (La,Sr)(Cr,Mn)O₃ (LSCM) were prepared using similar processing conditions. The LSCM powder was synthesized by the solid state reaction method. La₂O₃ (99.99%), SrCO₃ (99%), Cr₂O₃ (99%), and MnO₂ (99.9%) powders were weighed and mixed with water prior to ball milling for 24 hrs. After drying and grinding, the LSCM powder was calcined at 1500°C. All anodes were sintered at 1100°C for 3h.

To complete SOFCs, cathodes consisting of 50wt% of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{1.8} (LSCF) and 50wt% of GDC were applied to the other side of the electrolyte pellet. The cathodes were sintered at 900C for 3 h. These cathodes provide very low cathode polarization resistances even at relatively low temperatures.^{2,3} The anodes and cathodes were both about 30 μm thick and 6mm by 6 mm in area.

For impedance spectroscopy measurements and characterization of C deposition from various gases, the anodes were deposited on both sides of YSZ substrates.

B. Characterization

The anodes were characterized chemically using energy-dispersive x-ray analysis in an SEM, morphologically using a high-resolution field-emission SEM, structurally using x-ray diffraction, and electrically using van der Pauw measurements.

The initial measurements will be to expose the anodes to different fuel environments - i.e. wet and dry natural gas, methane, ethane, and propane - over a range of flow rates and temperatures. Carbon deposition was detected visually in some cases, and scanning electron microscopy (SEM) with energy-dispersive x-ray analysis was used for a more sensitive and quantitative measurement. This screening process was used to identify anodes for use in subsequent electrical testing described below.

Impedance spectroscopy measurements with an electrochemical interface were carried out to obtain an overall idea of the effectiveness of each anode.

Based on the above results, the best candidate anodes were incorporated into SOFCs. Single-cell SOFC tests were carried out over a range of temperatures from 500 to 800°C, and a range of cell voltages and current densities. Long-term measurements tested for the stability of anode electrochemical reactions. Degradation of cell performance over time was observed in some cases and related to changes in anode structure and/or carbon deposition.

Project Outcomes

Electrical resistivity measurements on Ni-Gd-doped Ceria (Ni-GDC) and Ru-GDC anodes with ≈ 50 vol% metal content have shown that they have the required conductivity. Initial structural evaluation using scanning electron microscopy has shown that the anodes have the desired porous structure, as shown in the image below (Fig. 1). Images from slurry-coated anodes look similar. Thus, both these methods provide a satisfactory anode structure.

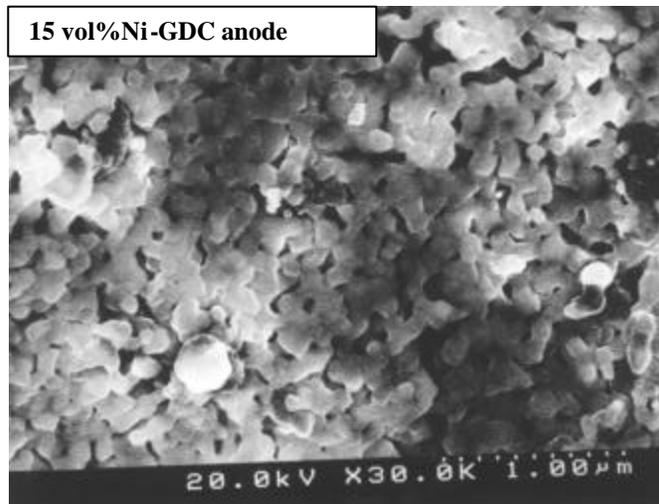


Figure 1. A SEM micrograph showing the structure of a Ni-GDC anode deposited by ultrasonic spray.

Tests for carbon deposition were completed. It was found that both the Ni-GDC and Ru-GDC anodes were able to work in methane without substantial carbon deposition. However, natural gas actually contains a few percent of higher hydrocarbons. Tests were therefore carried out with one of the more abundant of these hydrocarbons, propane. Here substantial carbon deposition was found on Ni-GDC, and somewhat less carbon deposition on Ru-GDC.

In order to avoid this carbon deposition, a third alternative anode material (that was not in the original statement of work) was tested. In this anode, the metal is replaced by an

electronically-conducting oxide (La,Sr)CrO₃. This supplies the required electrode conductivity, with the advantage that it does not promote carbon deposition like Ni and Ru. Initial tests showed that these anodes did not have significant carbon deposited after testing in propane. Some of these anodes were also made with a small amount (5 wt%) of Ni added. These also did not show significant carbon deposition.

Impedance spectroscopy and cell test measurements were carried out on these anodes. The Ni-GDC anodes yielded the best performance, with the (La,Sr)CrO₃-GDC-Ni anodes a close second. The Ru-GDC and (La,Sr)CrO₃-GDC (without Ni) were found to be inferior due to their higher polarization resistance (this will translate into a lower power density in fuel cells made from this material). Figure 2 shows an example of an impedance result for the (La,Sr)CrO₃-GDC-Ni anodes at different temperatures. The real-axis intercept shows the ohmic component of the cell resistance, due primarily to the thick GDC electrolyte. The size of the arc indicates the anode polarization resistance component of the cell. The results show that at higher temperatures, the cell performance was limited primarily by the electrolyte. At lower temperatures, the performance was limited primarily by the anode.

Based on the above, the final choice of the best anode material has been deferred until more cell testing can be carried out. The Ni-GDC appears to be a strong contender at the moment, although it still needs to be tested in actual natural gas fuel containing impurities. The (La,Sr)CrO₃-GDC-Ni anodes also appear to be a good candidate, as they can clearly be used with the various hydrocarbons present in natural gas. Thus, cell tests on natural gas will be made shortly to determine which of these is the optimal choice.

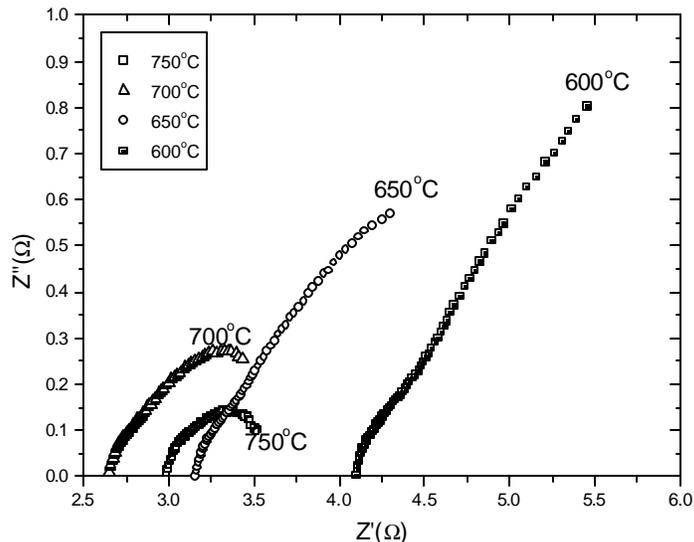


Figure 2. Representative impedance spectra measured at different temperatures from a SOFC with (La,Sr)CrO₃-GDC-Ni anode. Note that the resistance was higher at 750°C due to an experimental artifact – the lead wire became partially disconnected at this temperature.

Overall, the results indicated that Ru provided similar electrochemical performance to Ni, slightly reduced coking, but at a much higher cost. On the other hand, the anodes with reduced Ni content were most promising for reducing coking to a manageable level. However, at very low Ni content, there is insufficient conductivity in the Ni-Ceria anode. Thus, it was decided to attempt a new type of anode that was not included in the original proposed. In these anodes, the Ni content was reduced to very low levels (5 wt% compared to 70% in conventional anodes) and an electronically conducting ceramic that is known to not promote coking, LaCrO₃, was added. This combination of three different materials – electronically conducting ceramic, ionically conducting ceramic, and a metallic catalyst – has not been either suggested or utilized previously for SOFC electrodes. Indeed, almost all prior work focused on single-phase metallic or two-phase metal-oxide combinations, with the most common being Ni-YSZ.

The new anodes utilize $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$ (LSCM) as the electronically-conducting oxide. This oxide is used because it is an electronic conductor that is stable at high temperatures in a wide range of gas compositions. Sr and Mn dopants are common additions to LaCrO_3 that help match thermal expansion coefficient, increase the electronic conductivity, and improve the sinterability.⁴ Note that other LaCrO_3 dopants are possible and would likely also work for this application as long as they maintain good electronic conductivity. LaSrCrO_3 anodes have been studied previously for use as SOFC anodes with YSZ electrolytes,⁵ but have always provided large polarization resistances, and hence small power densities, because they are relatively poor catalysts for anode electrochemical reactions. In the present new anodes, we have mixed the LSCM electronic conductor with the ionically-conducting oxide $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC). This improves the adhesion on GDC electrolytes and improves the electrochemical performance by increasing the density of triple-phase boundaries. Ceria is also well known to promote hydrocarbon oxidation.⁶ A small amount (5wt%) of nanometer-scale Ni was added in some cases. This illustrates a key advantage of the new type of anode – since the metal acts only as the catalyst and is not required for current collection or structural support, its composition and amount can be varied in order to optimize electro-catalytic properties and minimize carbon deposition.

The cell testing phase was begun with both conventional Ni-GDC and the new (La,Sr)CrO₃-Ni-GDC anodes retained as candidates. After an initial assessment (results comparing the two anodes are shown below), a decision was made to concentrate on the latter anodes. These anodes show the most promise as their performance is comparable to the more conventional Ni-GDC anodes, and the risk of anode failure due to coking is minimized. Furthermore, as discussed below, the anodes can be repeatedly exposed to air without

degradation – this is important in case a break in fuel cell plant operation produces conditions for coking, since the carbon can then be removed by exposure to air. Furthermore, it will be desirable to cycle small power plants on and off, and exposure of the hot anode to air is likely as the power plant is shut down.

A. Comparison of LSCM-GDC-Ni and Ni-GDC anodes

SOFCs were prepared with Ni-GDC and LSCM-GDC-Ni anodes. The SOFCs were tested with air and a few representative fuels: H_2 (typically used in fuel cells), CH_4 (the most common gaseous fuel) and C_3H_8 (a common liquid fuel with very high energy density). Figure 3 illustrates typical SOFC current-voltage results taken for cells with LSCM-GDC-Ni and Ni-GDC anodes at $750^\circ C$ for hydrogen. The performance of the cells with the LSCM-GDC-Ni anodes was similar to the more typical Ni-GDC anodes. In fact, the maximum power density was only a few % less.

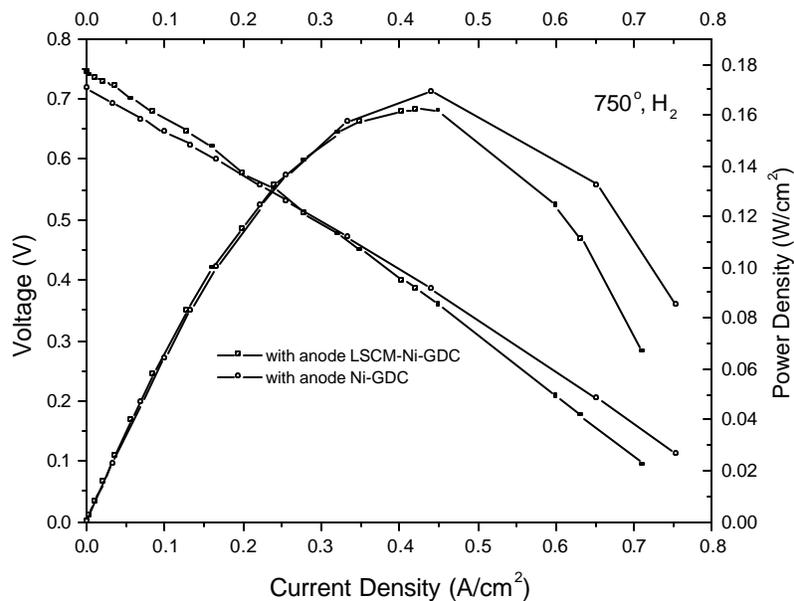


Figure 3. Performance comparison of identical SOFCs with LSCM-GDC-Ni and Ni-GDC anodes in air and H_2 at $750^\circ C$.

Impedance spectroscopy measurements were also carried out during the cell tests, in order to separate the cell resistances arising from the electrolyte and electrodes. The electrolyte ohmic resistance measured at 750°C was 0.49 Ωcm^2 . This value is in good agreement with the electrolyte ohmic loss expected for 0.5 mm thick GDC. Note that this same value applies for all of the 750°C results shown below, as the electrolyte composition and thickness was the same in all cases. For the LSCM-GDC-Ni anode cell shown in Fig. 3, the anode plus cathode polarization resistance was 0.44 Ωcm^2 , or 47% of the cell resistance.

Figure 4 shows the results for these same cells operated with propane as the fuel. Unlike Fig. 3, the power density with the LSCM-GDC-Ni anodes is actually larger than for Ni-GDC. Furthermore, there was no carbon deposition detected on the ceramic anodes when the cells were operated for several hours at the maximum power point or higher currents. Figure 5a shows a typical SEM/EDX result indicating no detectable carbon. The same cells maintained at open-circuit condition in propane for > 3 hrs showed no visual evidence of carbon deposition, but SEM/EDX revealed a small amount of C (Fig. 5b). It should be noted that LSCM-GDC anodes showed nearly identical SEM/EDX results, indicating that the 5% Ni in the anodes had little influence on carbon deposition. On the other hand, the Ni-GDC anodes showed heavy carbon deposition (gram quantities) after running the cells on propane, even with the cells maintained at short circuit condition. These results indicate that ceramic-based anodes with ≈ 5 wt% Ni work quite well with heavy hydrocarbon fuels, under conditions where conventional SOFC anodes containing much larger amounts of Ni, i.e. ≈ 50 wt%, provide lower power and fail rapidly.

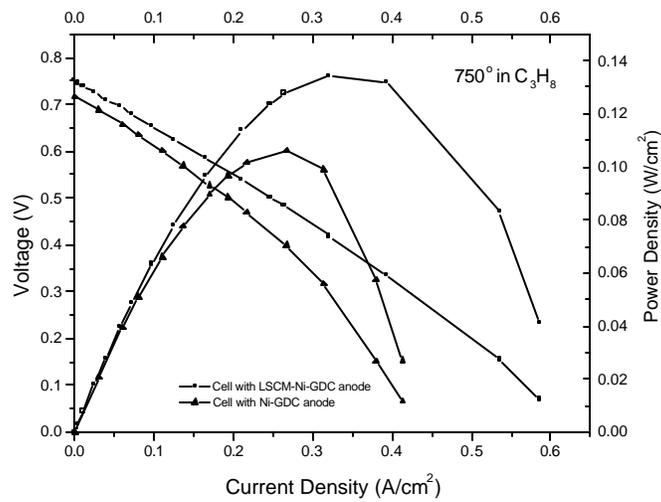


Figure 4. Performance of SOFCs with LSCM-GDC-Ni and Ni-GDC anodes operated in air and C₃H₈ at 750°C.

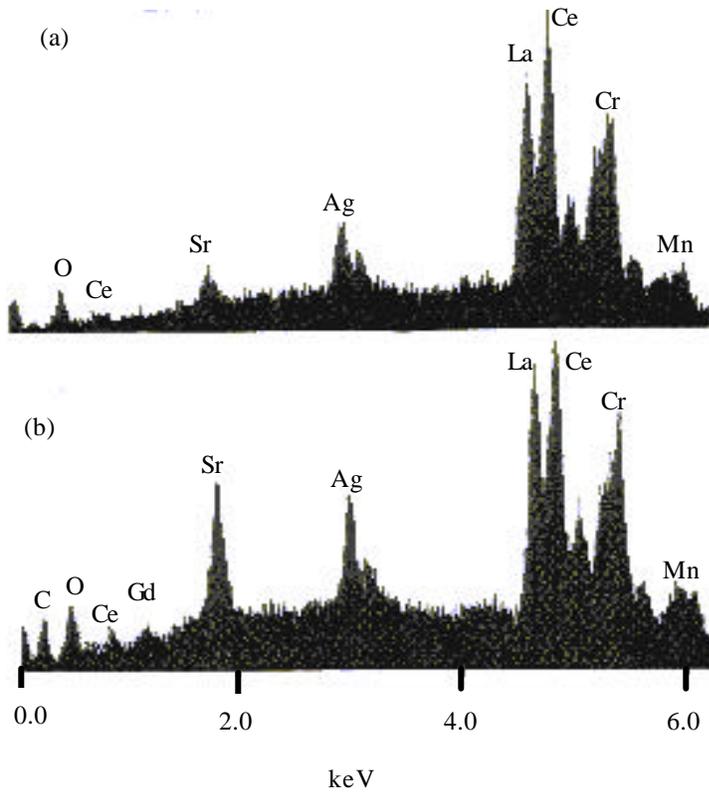


Figure 5. SEM/EDX scans of LSCM-GDC-Ni anodes after cell testing in humidified propane for 200 mins at 750°C under (a) short circuit conditions and (b) open circuit conditions.

B. Effect of Ni in LSCM-GDC anodes

Figure 6a shows the SOFC characteristics for the LSCM-GDC-Ni anode with the methane as the fuel, compared to hydrogen. The performance with methane was not as good as with hydrogen, with an $\approx 20\%$ lower power density. This is similar to prior reports on SOFCs with Ni-YSZ-Ceria anodes operated on both hydrogen and methane. Figure 6b shows the cell test results obtained when LSCM-GDC (no Ni) was used as the anode with methane as the fuel. In addition to providing a lower current density, the open circuit potential (OCP) was substantially less. As a result, the maximum power density was substantially reduced, from 125 to 50 mW/cm^2 . Additional results comparing anodes with and without Ni tested with propane are shown in Figure 7. For both temperatures tested, the cells performed much better for the anodes with Ni, providing both higher OCPs and higher current densities.

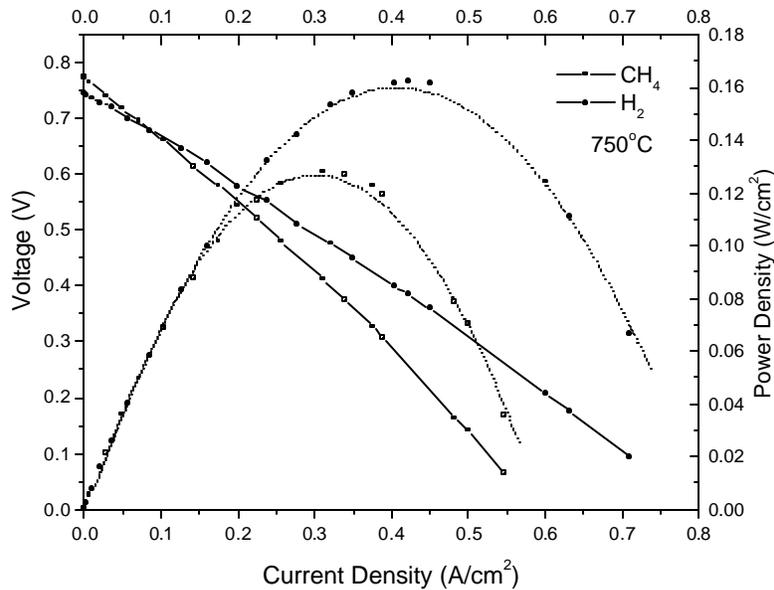


Figure 6a. The characteristics of the fuel cell LSCM-Ni-GDC/GDC/LSCF-GDC in CH_4 compared with H_2 .

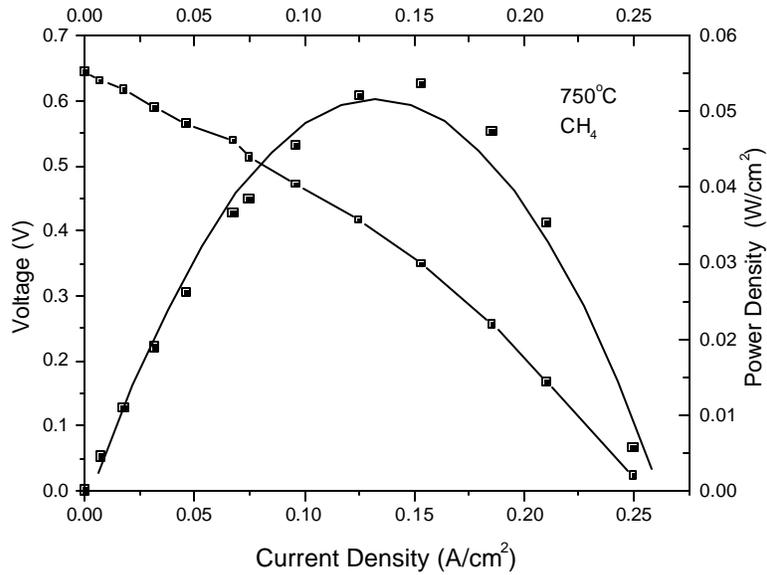


Figure 6b. The performance of a LSCM-GDC(without Ni)/GDC/LSCF-GDC fuel cell in CH₄ at 750°C.

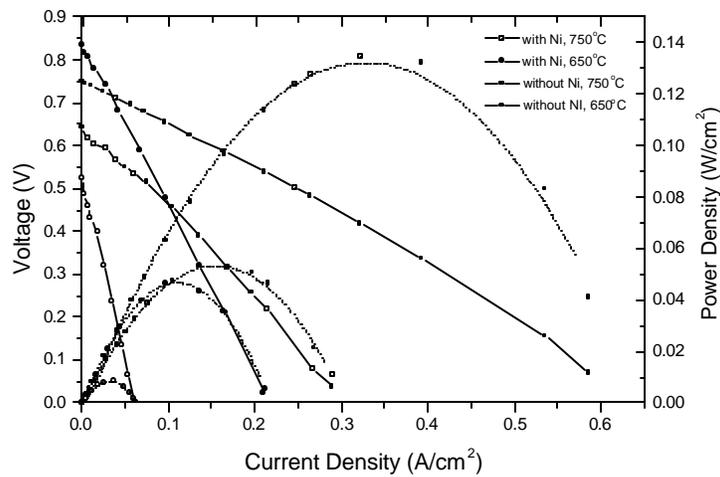


Figure 7. Performance of SOFCs with Ni-free and Ni-containing anodes in air and propane.

The above results show the importance of adding a small amount of metal catalyst for obtaining good anode electrochemical performance. This also agrees with prior reports where it was shown that both LaCrO₃ and GDC were relatively poor anode electro-catalysts by themselves.^{5,7}

C. Effect of reduction-oxidation cycling

Another important aspect of the new ceramic-based anodes is that they are relatively stable over a range of fuel-gas compositions. It is well known that repeatedly cycling Ni-YSZ anodes between oxidizing and reducing atmospheres has a deleterious effect on their performance, presumably because of the substantial volume change upon oxidation of Ni.⁸ This is probably because Ni, with a content of $\approx 50\%$, is a primary structural component; thus, the large volume changes upon oxidation and reduction may damage the structure. Because of the interest in their stability, the performance of ceramic-based anodes after reduction-oxidation (redox) cycling was investigated. Figure 8 shows the performance on hydrogen over a range of temperatures for an anode that had been redox cycled four times between air and H₂ (with 3% H₂O), for 30 mins in each exposure, at 750°C. For comparison, the performance of an identical cell prior to redox cycling is shown in Fig. 9. The performance is actually slightly improved after cycling. Figure 10 shows a comparison of the performance on propane at 750°C before and after the same redox cycling procedure. As can be seen, the performance is, if anything, increased after cycling. The improvements shown in Figs. 8-10 may be artifacts, not due to the redox cycling but rather due to slight cell-to-cell variations.

The present anodes may be more stable than Ni-YSZ anodes because the predominant LSCM and GDC phases exhibit only minor volume changes upon reduction and oxidation. While the Ni in these anodes will oxidize and reduce, the amount of Ni is quite small such that little effect on the anode structure is expected.

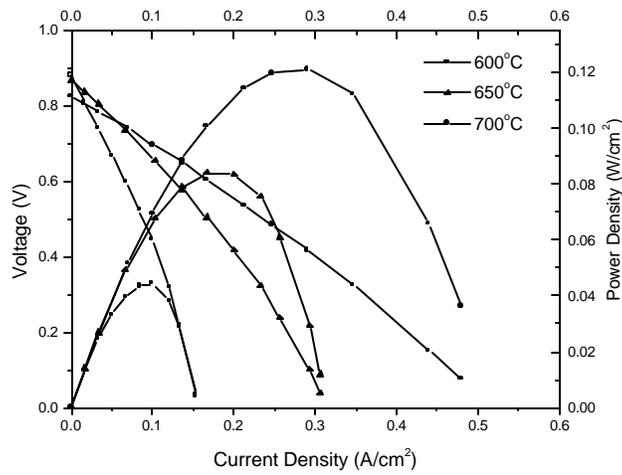


Figure 8. Performance a SOFC with a LSCM-GDC-Ni anode after redox cycling between air and H₂

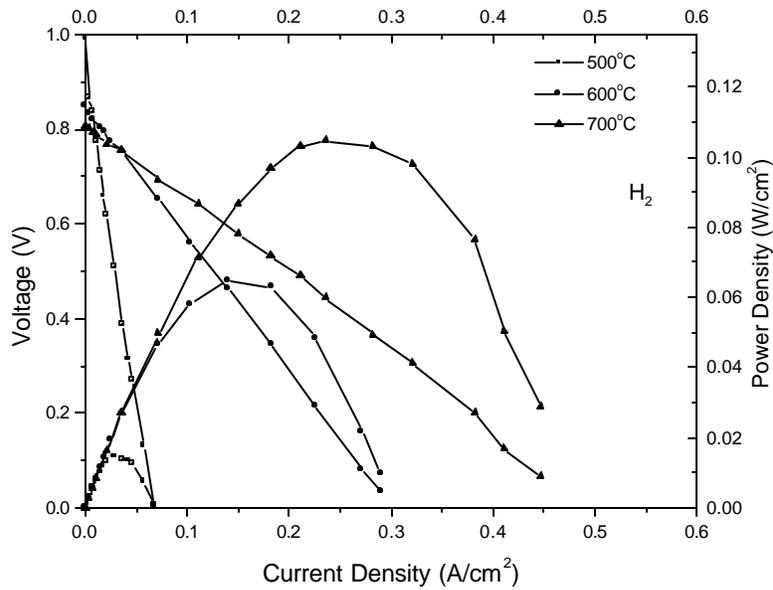


Figure 9. Performance a SOFC with a LSCM-GDC-Ni anode that had not been exposed to redox cycling.

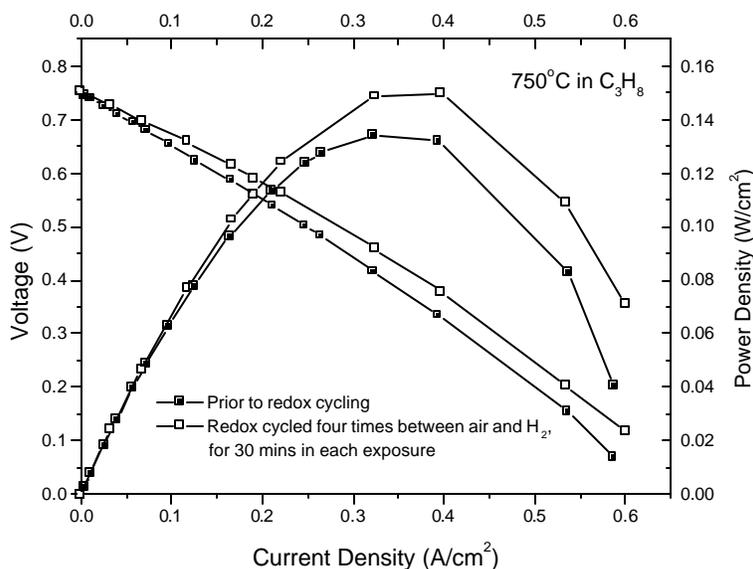


Figure 10. Performance of the redoxed fuel cell in propane at 750°C compared with the non-redoxed fuel cell.

Note that in all of the cell performance results in this report, the open-circuit potential is rather low, 0.7-0.85V. For the current test conditions in hydrogen, an OCP of 1.1V is expected theoretically. For methane and propane, the OCP is not well defined. Prior work with methane has shown OCP values of ≈ 1 V. However, there are no prior reports of OCP values for propane. The present low OCP values result because of the electronic conductivity in the GDC electrolyte at this temperature. While this reduces cell efficiency, it is essentially an artifact of the present tests. In practice, these anodes would be used in SOFCs with thin GDC or YSZ electrolytes. For thin GDC electrolytes, lower operating temperatures should be achieved where the electronic conductivity is substantially decreased. For thin YSZ electrolytes, good OCP values are obtained.

The only other example of SOFCs that can operate with a wide range of fuels without carbon deposition while providing reasonable power densities, are recent reports by the Univ. of Pennsylvania group. In these studies, novel Cu-GDC anodes were used. The power densities obtained with the present cells were similar to those obtained with the Cu-based anodes under similar operating conditions. Each of these anodes may have different advantages and disadvantages. Cu has the advantage of providing quite high conductivity, much higher than LSCM, which is advantageous for current collection. On the other hand, the melting points of

Cu and Cu₂O are relatively low, limiting processing temperature to unusually low values, and raising questions about the long-term stability of the anodes. The present ceramic-based anodes are readily processed at typical SOFC processing temperatures, and are likely stable for long times. Like Ni-YSZ anodes, Cu-GDC anodes may be susceptible to degradation upon redox cycling because of volume changes; as shown above, the present ceramic anodes appear to be unaffected by cycling.

Primddahl *et al*⁵. considered doped LaCrO₃ anode materials for SOFCs with a yttria-stabilized zirconia (YSZ) electrolyte. These anodes yielded relatively high anode polarization resistance at 850°C operated with hydrogen, 2 – 5 Ω cm², and the resistance increased gradually with time. The addition of a small amount of Ni yielded a substantial reduction in polarization resistance from 5 to 2 Ω cm². The present results show a marked improvement over prior reports, even at a substantially lower temperature (750 versus 850°C), with a polarization resistance of < 0.5 Ω cm² (see Fig. 3). The present anodes also gave quite good performance with methane and propane fuels. In contrast, with methane fuel, LaCrO₃-based anodes showed relatively poor catalytic activity for electrochemical oxidation and reforming reactions⁵, along with high polarization resistances.⁴ We believe that the present good results are not due to the specific chromate composition used, but rather to the combination of electronically and ionically conducting materials with a catalyst.

Studies of Ceria anode performance have also shown promising results, indicating electrochemical methane oxidation without C deposition at 800⁹ and 900°C,¹⁰ but yielding quite low SOFC power densities.⁹ However, a recent report has shown poor activity for electrochemical oxidation of methane for ceria when combined with a relatively inert metal current collector, i.e. Au. In other studies where a more catalytically active current collector, e.g. Pt, was used, much better performance was achieved with methane at 800-1015 °C.¹¹ This again supports our contention that it is necessary to combine an ionically-conducting material such as ceria with a catalyst and current collector to make an effective hydrocarbon anode.

Conclusions

- We have characterized anode reactions using scanning electron microscopy to detect carbon deposition, impedance spectroscopy with an electrochemical interface, and SOFC current-voltage measurements.
- This project has verified the feasibility of operating solid-oxide fuel cells (SOFCs) directly on natural gas.
- We have determined conditions where the fuel cell can be operated using de-sulfurized natural gas without carbon deposits on the anode.
- We also tested SOFC performance on higher-hydrocarbon components of natural gas, and it has shown that the cells can be operated with other fuels such as propane.
- After testing Ni-Ceria and Ru-Ceria anodes, it was determined that anodes with very low Ni content, using a ceramic conductor to provide anode conductivity, yielded good performance. That is, they provided fast electrochemical oxidation, and hence high power densities, without carbon deposition.

It should also be noted that this general anode approach provides great flexibility for improving performance, since the relative amounts and the chemical nature of each of the three phases can be altered to match a specific fuel or operating condition. A major additional advantage of the new anodes is that they can be cyclically reduced and oxidized without degrading performance. This redox cycling is expected to occur regularly on periodic shutdown of small generators when the fuel flow is stopped. Thus, the present SOFC anodes may help to make possible new applications of SOFCs that rely on the direct use of high energy density hydrocarbon fuels and feature frequent on-off cycling, such as portable power, auxiliary power units used in transportation, and distributed generation. While our early stability tests of these anodes are promising, longer-term tests are needed.

Finally, the effects of sulfur-containing compounds on these anodes are as yet unknown. We suggest that the effect of sulfur on these anodes will probably be similar to that observed for conventional Ni-YSZ anodes, since Ni still plays a key role. However, experimental are clearly required to test this.

Recommendations

In order to advance this technology towards commercialization, we believe that a few key steps need to be taken. First, there needs to be a fairly sizable R&D effort carried out to improve and optimize the structure and composition of the new anodes for use with natural gas. The effects of sulfur-containing compounds should be assessed, in order to determine whether a sulfur cleanup step will be required for the SOFC generators. At the same time, the long-term behavior of SOFCs incorporating these anodes should be investigated. The anode development work should include as one of the criteria that the anodes achieve stable long-term performance. In addition, the long-term test should include frequent cycling of operating conditions, including exposure to air, as expected in the real operation of small SOFC generators. Finally, the anodes should be used as the support element of thin-electrolyte SOFCs; this will not only provide the best overall performance, but it matches the SOFC configuration being commercially developed. If these anodes can be incorporated into this existing scheme, this will maximize the commercial prospects for this new anode technology.

Public Benefits to California

The only benefits that California has already received from this contract are its rights to the SOFC anode invention disclosed based on this project. The benefits to California of the widespread use of SOFC technology would be a cleaner, more efficient electrical energy generation network. Because of the ability to site SOFC generators essentially anywhere, and the fact that they can be any size, it will be possible to produce a highly robust, flexible, and adaptable distributed generation system that will serve California ratepayers well.

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