U.S. DEPARTMENT OF ENERGY

FINAL REPORT

Report Title: Development of Low-Cost Manufacturing Processes for Planar, Multilayer Solid Oxide Fuel Cell Elements

Type of Report: Final Report

Reporting Period Start Date: June 13, 2000

Reporting Period End Date: June 12, 2004

Principal Authors: Scott Swartz (a); Matthew Seabaugh (a); William Dawson (a); Harlan Anderson (b); Tim Armstrong (c); Michael Cobb (d); Kirby Meacham (d); James Stephan (e); Russell Bennett (f); Bob Remick (g); Chuck Sishtla (g); Scott Barnett (h); and John Lannutti (i).

Date of Report: June 12, 2004

DOE Contract Number: DE-AC26-00NT40706

Submitting Organizations: NexTech Materials, Ltd. (a); University of Missouri-Rolla (b); Oak Ridge National Laboratory (c); Michael A. Cobb & Co. (d); Advanced Materials Technologies, Inc. (e); Edison Materials Technology Center (f); Gas Technology Institute (g); Northwestern University (h); and The Ohio State University (i).

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

This report summarizes the results of a four-year project, entitled, *Low-Cost Manufacturing Of Multilayer Ceramic Fuel Cells*, jointly funded by the U.S. Department of Energy, the State of Ohio, and by project participants. The project was led by NexTech Materials, Ltd., with subcontracting support provided by University of Missouri-Rolla, Michael A. Cobb & Co., Advanced Materials Technologies, Inc., Edison Materials Technology Center, Gas Technology Institute, Northwestern University, and The Ohio State University. Oak Ridge National Laboratory, though not formally a subcontractor on the program, supported the effort with separate DOE funding. The objective of the program was to develop advanced manufacturing technologies for making solid oxide fuel cell components that are more economical and reliable for a variety of applications. The program was carried out in three phases. In the Phase I effort, several manufacturing approaches were considered and subjected to detailed assessments of manufacturability and development risk. Estimated manufacturing costs for 5-kW stacks were in the range of \$139/kW to \$179/kW. The risk assessment identified a number of technical issues that would need to be considered during development. Phase II development work focused on development of planar solid oxide fuel cell elements, using a number of ceramic manufacturing methods, including tape casting, colloidal-spray deposition, screen printing, spin-coating, and sintering. Several processes were successfully established for fabrication of anode-supported, thin-film electrolyte cells, with performance levels at or near the state-of-the-art. The work in Phase III involved scale-up of cell manufacturing methods, development of non-destructive evaluation methods, and comprehensive electrical and electrochemical testing of solid oxide fuel cell materials and components.

TABLE OF CONTENTS

Abstract	2
Table of Contents	3
Introduction	8
Executive Summary	9
Phase I: Manufacturing Cost Analysis and Risk Assessment	11
Phase I Overview	11
Phase I Methodologies	12
Cost Estimation Approach	13
Risk Assessment Approach	16
Phase I Results and Discussion	19
Co-Sintered Planar Thin-Film Electrolyte Elements (NexTech and ORNL)	19
Ultra-Thin Electrolyte (University of Missouri–Rolla)	22
Co-Extrusion of Electrolyte Elements (Adaptive Materials, Inc.)	25
Results of Cost Estimation	29
Results of Risk Assessment	33
Technical Risk Associated with Development	33
Technical Risk Associated with Sealing and Manifolding	33
Phase I Conclusions	37
Phase II: Development of SOFC Manufacturing Processes	38
Phase II Overview	38
Phase II Results and Discussion (NexTech, Track 1)	40
LSM Powder Production	40
Fabrication of LSM Cathode Substrates	40
Interlayer Material Selection	45
Electrolyte Coating Process Development	49
Fabrication of Cathode-Supported Planar Elements	51
Fabrication of Anode-Supported Planar Elements	57
Screen Printing Process Development	58
Nano-Composite Anode and Cathode Powders	59
Phase II Results and Discussion (ORNL, Track 2)	61
Anode Support Development (Organic System)	61
Anode Support Development (Aqueous System)	62
Screen Printing Development (Electrolyte)	63
Screen Printing Development (Catalytic Layers)	65
Process Flow Diagram	65

Phase II Results and Discussion (UMR, Track 3)	68
Porous LSM Cathode Substrate Preparation.....	68
LSM Layers with Fine-Scale Porosity	71
Bi-layer Cathode Substrates.....	73
Ceria Interlayer and YSZ Electrolyte Films	75
Phase II Conclusions.....	79
Phase III: Scale-Up and Comprehensive Testing	81
Phase III Overview	81
Phase III Results and Discussion	81
Cathode Supported Cells.....	81
Screen-Printed Cathode Coatings	83
Fabrication of Anode-Supported Cells	88
Button-Cell Testing.....	97
Single-Cell Testing of Large-Area Cells	106
Non-Destructive Testing.....	113
Mechanical Property Testing	119
Phase III Conclusions	119
List of Acronyms and Abbreviations.....	120
Appendices.....	121

LIST OF TABLES

Table 1.	Description of manufacturing approaches and designs	11
Table 2.	Summary of cost estimation and risk assessment results	12
Table 3.	Pairwise Comparison Scale (for assessing risk)	18
Table 4.	Ranking of Evaluation Criteria.....	19
Table 5.	Advantages of Development Approaches	20
Table 6.	Design Parameters for Cost Estimation.....	30
Table 7.	Estimated Stack Costs and Performance Ratios	30
Table 8.	Assessment of Development Risk	33
Table 9.	Assessment of Risk Associated with Sealing and Manifolding	33
Table 10.	Technical Rationale behind Risk Assessment Results	34
Table 11.	Technical Challenges and Development Approaches	39
Table 12.	Results of Reaction Studies	46
Table 13.	Summary of Electrode Resistance Measurements.....	88
Table 14.	Evolution of NexTech's process development efforts for anode-supported cells.....	90
Table 15.	SOFC performance data obtained using button-cell testing methods	98
Table 16.	Ranking of cathode performance based on button-cell test results	97

LIST OF FIGURES

Figure 1.	Methodologies used for estimating cell and stack manufacturing costs.....	14
Figure 2.	Pro-forma stack design used for estimating planar SOFC stack costs	15
Figure 3.	Fabrication process for cathode-supported, thin-film electrolyte SOFCs	21
Figure 4.	Schematic of co-sintered cathode/interlayer/electrolyte elements	22
Figure 5.	Cathode-supported Quadrilayer SOFC element	23
Figure 6.	Anode-Supported Quadrilayer structure.....	24
Figure 7.	Quadrilayer SOFC module	25
Figure 8.	Pictorial example depicting MCFX fabrication process.....	26
Figure 9.	Examples of components fabricated by MFCX.....	27
Figure 10.	SEM micrograph of MCFX-fabricated tubular SOFC element.....	29
Figure 11.	Breakdown of stack manufacturing cost by category.....	31
Figure 12.	Breakdown of stack manufacturing cost by material type.....	31
Figure 13.	Unit operations required for fabrication of planar SOFC elements.....	38
Figure 14.	XRD pattern of phase-pure lanthanum strontium manganite powder	41
Figure 15.	Particle size distribution of LSM powder.....	41
Figure 16.	Electrical conductivity data for various perovskite cathode materials	42
Figure 17.	Optical profilometry scans showing curvature in sintered LSM laminates.....	43
Figure 18.	Optical profilometry of sintered LSM substrate.....	44
Figure 19.	SEM micrograph of polished surface of porous LSM substrate.....	44
Figure 20.	X-ray diffraction pattern of phase-pure PSMF-8255 powder.....	46
Figure 21.	XRD pattern of mixture of LSM and YSZ, sintered at 1350°C.....	47
Figure 22.	XRD pattern of mixture of LSM and GDC, sintered at 1350°C.....	47
Figure 23.	XRD pattern of mixture of PSMF and YSZ, sintered at 1350°C.....	48
Figure 24.	XRD pattern of mixture of PSMF and GDC, sintered at 1350°C.....	48
Figure 25.	Particle size distributions of aqueous nanoscale YSZ suspensions	49
Figure 26.	Ultrasonic-spray deposition system used for depositing YSZ electrolyte coatings ...	50
Figure 27.	NexTech's multilayer ceramic fabrication clean-room facility	50
Figure 28.	Laser dilatometry of LSM laminates during sintering.....	52
Figure 29.	Laser dilatometry of LSM laminates during sintering.....	52
Figure 30.	Laser dilatometry of uncoated and YSZ-coated LSM laminates during sintering	53
Figure 31.	SEM micrographs of PSMF/GDC interlayer coating.....	54
Figure 32.	Optical profilometry scan showing surface topography of interlayer coating	55
Figure 33.	As-deposited and sintered films of YSZ on porous LSM substrates.....	55
Figure 34.	SEM micrograph of a fractured cross-section of a cathode-supported element.....	56
Figure 35.	Optical profilometry scans of co-sintered cathode-supported SOFC element	56
Figure 36.	SEM micrograph of a polished cross-section of an anode-supported element.....	57

Figure 37. SEM micrograph of a polished cross-section of an anode-supported element.....	58
Figure 38. SEM micrographs of NiO/YSZ anode powder mixtures.....	60
Figure 39. Cross-sectional SEM micrographs of anodes substrates	61
Figure 40. Cross-sectional SEM micrographs of anodes substrates	62
Figure 41. Screen printed and sintered YSZ electrolyte film on anode substrate	63
Figure 42. Screen printed and sintered YSZ electrolyte films on anode substrates.....	64
Figure 43. Anode with screen printed YSZ layer, before and after sintering at 1400°C.....	65
Figure 44. Anode-supported cell with functional interlayers.....	66
Figure 45. Screen printed and sintered ceria interlayer on YSZ electrolyte	66
Figure 46. Process flow diagram for manufacture of anode supported cells at ORNL	67
Figure 47. Characterization of NexTech-supplied LSM powder.....	69
Figure 48. SEM characterization of carbon fugitive powders	69
Figure 49. Density versus sintering temperature for LSM substrates	70
Figure 50. SEM micrographs of sintered LSM tapes, without carbon fugitive	70
Figure 51. SEM micrographs of sintered LSM tapes, with carbon fugitive	71
Figure 52. The accumulation pore volume of LSM tapes with fine-scale carbon fugitive.....	72
Figure 53. SEM micrographs of LSM tapes with fine-scale carbon fugitive	72
Figure 54. SEM micrographs of LSM tapes with fine-scale carbon fugitive	73
Figure 55. SEM micrograph of cross section of sintered bi-layer LSM substrate.....	74
Figure 56. SEM micrograph of classified carbon fugitive particles	74
Figure 57. SEM micrographs LSM tape prepared with classified carbon fugitive.....	75
Figure 58. SEM micrograph of double-layer cathode substrate	76
Figure 59. Schematic of process for nano-crystalline ceria interlayer films.....	76
Figure 60. Ceria interlayer films deposited on porous LSM cathode substrates	77
Figure 61. Ceria interlayer films deposited on porous LSM cathode substrates	77
Figure 62. YSZ electrolyte film on LSM substrate with a nano-porous ceria interlayer.....	78
Figure 63. Top surfaces of ceria interlayer and YSZ electrolyte films.....	78
Figure 64. SEM/EDS data obtained on cathode-supported YSZ electrolyte film	82
Figure 65. Screen printing of composite cathodes	83
Figure 66. Electrical conductivity of single-phase perovskite electrode materials.....	84
Figure 67. SEM and BSE micrographs of screen-printed composite cathode coatings.....	84
Figure 68. Specific electrode resistances for LSF-40 and LSF/GDC cathode coatings	86
Figure 69. Specific electrode resistances for LSCF and LSCF/GDC cathode coatings	86
Figure 70. Specific resistance of LSCF/GDC electrodes, measured by different methods	87
Figure 71. Effect of calcination on interfacial resistance of composite cathodes	87
Figure 72. Fabrication methods used in the production of anode-supported cells.....	89
Figure 73. Effect of lamination method on morphology of sintered anode substrates	91

Figure 74. Effect of tape casting formulation on the morphology of anode substrates	91
Figure 75. Effect of lamination conditions on morphology of sintered anode substrates.....	92
Figure 76. Effect of different pore formers on morphology of sintered anode substrates	92
Figure 77. Microstructure of porous anode substrates produced without pore formers	93
Figure 78. Shrinkage versus sintering temperature for different anode substrates	93
Figure 79. Control of sintering shrinkage by pre-calcination of anode substrates.....	94
Figure 80. Anode-supported YSZ electrolyte films made with different YSZ powders	95
Figure 81. Anode supported cell with screen printed ScSZ electrolyte film	96
Figure 82. Anode supported cell with screen printed ScSZ electrolyte film	96
Figure 83. SOFC performance data	102
Figure 84. SOFC performance data	102
Figure 85. SOFC performance data	103
Figure 86. SOFC performance data	103
Figure 87. SOFC performance data	104
Figure 88. SOFC performance data	104
Figure 89. SOFC performance data	105
Figure 90. SOFC performance data	105
Figure 91. Single-Cell testing methodology used at GTI for large-area cells	107
Figure 92. Post-mortem cell evaluations.....	108
Figure 93. Cell performance data obtained at GTI on large-area anode supported cells.....	109
Figure 94. Single-Cell testing methodology used at NexTech for large-area cells	110
Figure 95. SOFC performance measured at NexTech for large-area cell.....	111
Figure 96. SOFC performance measured at NexTech for large-area cell.....	111
Figure 97. SOFC performance measured at NexTech for large-area cell.....	112
Figure 98. Optical profilometry image showing curvature of anode-supported cell	113
Figure 99. Optical profilometry image showing defects in electrolyte film	114
Figure 100. Optical profilometry scans of anode-supported cells	115
Figure 101. Schematic diagram of the laser dilatometer used at Ohio State University	116
Figure 102. Three-dimensional reconstruction of a SOFC laminate at 1304°C	117
Figure 103. Laser dilatometry analysis of a model “stack” during heating	118
Figure 104. Dimensional change of an individual seal	118

INTRODUCTION

Fuel cells generate power by extracting the chemical energy of natural gas or other hydrogen-containing fuels without combustion. Advantages include high efficiency and very low release of polluting gases (e.g., NO_x) into the atmosphere. The solid oxide fuel cell (SOFC) offers advantages of high efficiency, low materials cost, minimal maintenance, and direct utilization of various hydrocarbon fuels without external reforming. Solid oxide fuel cells operating with natural gas as a fuel at temperatures of 800 to 1000°C can achieve power generation efficiencies in the range of 40 to 45 percent. Hybrid systems combining solid oxide fuel cells and gas turbines can achieve efficiencies of up to 70 percent. Materials technology for high-temperature SOFCs has been demonstrated in tubular systems being developed by Siemens-Westinghouse Power Corporation. These systems operate at temperatures of 950 to 1000°C, with exceptionally low degradation rates observed over thousands of hours of operation. However, the high cost of these systems (more than \$1,500/kW) has limited applicability to very large-scale (megawatt) stationary power applications. However, the use of SOFCs in mass-market applications, such as residential heat and power and automotive auxiliary power units, requires smaller-scale systems (3-10 kW) that can be mass-produced at a target cost of \$400/kW. The focus of this project was on development of ceramic manufacturing technology for planar SOFC components with high power density and low operating temperature, with the primary aim of reducing cost of SOFC systems.

The ceramic materials used in high-temperature solid oxide fuel cells based on current planar and tubular designs are essentially defined. Yttrium-stabilized zirconia (YSZ) is the most widely used ceramic electrolyte membrane material. The anode material is a porous Ni-YSZ cermet, and the cathode material is a porous $(\text{La,Sr})\text{MnO}_3$ (LSM) ceramic. Current designs involve the use of relatively thick YSZ membranes, which require relatively high operating temperatures (900~1000°C) to achieve optimum performance. Approaches to reduce SOFC operating temperature all begin with reduction of the electrolyte resistance, which can be achieved by: (1) using thin-film YSZ electrolyte membranes; or (2) replacing YSZ with a higher-conductivity ceramic electrolyte material. More substantial reductions in operating temperature can be achieved by combining both of these approaches. However, reducing the electrolyte resistance alone is not sufficient. The anode and cathode materials must be re-engineered to provide the required electrochemical performance at low temperatures, mutual compatibility of the new materials must be established, and cell designs and stack configurations incorporating the new materials must be developed.

The project was carried out in three phases. In Phase I, several manufacturing approaches were considered and subjected to detailed assessments of manufacturability and development risk. Phase II focused on development of electrode-supported, planar solid oxide fuel cell elements of thin-film electrolyte configurations, using a number of manufacturing methods, including tape casting, lamination, aerosol-spray deposition, screen printing, spin-coating, and sintering. The work in Phase III involved scale-up of cell manufacturing methods, development of non-destructive evaluation methods, and comprehensive electrical and electrochemical testing of solid oxide fuel cell materials and components.

EXECUTIVE SUMMARY

This four-year, collaborative development project was aimed at the development of low-cost ceramic manufacturing processes for planar solid oxide fuel cell elements. NexTech Materials led the project, and team members included University of Missouri-Rolla (UMR), Michael A. Cobb & Co. (MAC), Advanced Materials Technologies (AMT), Edison Materials Technology Center (EMTEC), Gas Technology Institute (GTI), Northwestern University, The Ohio State University, and Oak Ridge National Laboratory (ORNL).

In Phase I of this project, completed in October of 2000, stack manufacturing cost and development risk were assessed for four different solid oxide fuel cell (SOFC) design and fabrication approaches:

- (1) Planar stacks of cathode-supported elements made using NexTech's tape casting, aerosol spray deposition, co-sintering and screen printing methods (baseline);
- (2) Planar stacks of anode-supported planar elements made using ORNL's tape casting, screen printing and co-sintering methods (baseline);
- (3) Planar stacks of cathode-supported elements made by UMR's tape casting, spin-coating and screen printing methods (Option 1);
- (4) Planar stacks of anode-supported planar elements made using AMI's's co-extrusion methods (Option 2); and
- (5) An advanced (monolithic) cell/stack based on MAC's proprietary design (for comparison only).

The stack cost analysis, led by MAC, was based on the assumption of a 400-MW production facility, and a *pro forma* stack design with metallic interconnects. Projected costs range from \$139/kW to \$179/kW for planar designs, and \$94/kW for the advanced cell/stack design. The risk assessment, led by AMT, identified sealing and metallic interconnects as primary technical risks associated with development of planar cell/stack designs. This assessment also identified a number of technical issues that were used to guide development work. Based on the results of Phase I, three of the above-listed design/fabrication approaches (or tracks) for planar SOFC elements were selected for development in Phase II and testing in Phase III. These included the baseline tracks (led by NexTech and ORNL) and the Option 1 track (led by UMR).

The focus of Phase II, completed in October of 2001, was on the development of fabrication methods for planar cells. The work was highly collaborative, with NexTech and UMR working together on cathode substrate fabrication, NexTech and Ohio State collaborating on co-sintering processes, and NexTech and ORNL collaborating on screen-printing processes. NexTech developed fabrication processes for cathode-supported planar SOFC elements, based on tape casting of cathode (LSM) or anode (NiO/YSZ) substrates, aerosol spray deposition of the YSZ electrolyte films, co-sintering of anode/YSZ elements, and screen printing of cathode layers. ORNL developed a similar fabrication process for anode-supported cells, except that YSZ films were deposited by screen printing (rather than aerosol spray) prior to co-sintering. UMR's process development work focused on a novel spin-coating approach for depositing ultra-thin, nano-crystalline YSZ electrolyte films on pre-sintered cathode substrates. Specific fabrication challenges addressed included matching of shrinkages during co-sintering, controlling porosity

and morphology of sintered electrode substrates, and maintaining required flatness of co-sintered elements. Laser dilatometry and optical profilometry methods were established at Ohio State to monitor sintering shrinkages and for characterizing flatness and surface topology of sintered substrates and co-sintered elements. Several important fabrication process variables were identified that are critical to ultimate success in the high yield, low-cost manufacture of anode-supported solid oxide fuel cell elements with performance required for commercial applications. These include the following: controlling green density and sintering shrinkage of anode substrates; optimizing the tape casting and lamination processes to achieve ultimate uniformity of green density of anode substrates; deposition of electrolyte films with high green density to minimize shrinkage and assure high sintered density; optimizing co-sintering cycles to accommodate sintering shrinkage and thermal expansion mismatches; optimizing composition and processing of cathode materials, so that high performance can be retained when cathode coatings are applied by low-cost screen-printing methods; and performing critical fabrication operations in a clean environment.

Phase III of the project, completed in June of 2004, involved fabrication of appropriate SOFC samples and comprehensive characterization and testing of planar SOFC elements. Most of the work in Phase III was focused on anode-supported SOFCs. NexTech extended its cell fabrication processes to anode-supported cells, and scaled-up its fabrication processes to produce planar cells with up to 100-cm² areas. Screen printing methods also were established at NexTech for a range of low-temperature cathode formulations. "Button-cell" testing was performed at Northwestern to assess performance of SOFC samples prepared with different materials and fabrication methods. State-of-the-art levels of power density (>1 W/cm² at 800°C) were achieved for anode-supported cells produced at NexTech and at ORNL. Large-area, single-cell tests were conducted at GTI and at NexTech to assess performance of planar cells under application-specific conditions (i.e. high fuel and air utilizations). With the single-cell testing methods used, flatness was a critical issue, especially for anode-supported cells. Thus, a significant amount of effort in Phase III was focused on refining the cell fabrication methods to reduce cell camber and allow these tests to be completed. NexTech established a number of electrical and electrochemical testing methods, including ionic conductivity measurements, half-cell electrode resistance measurements, ac impedance spectroscopy, and single-cell SOFC tests. The ultimate result of single-cell testing was the demonstration of respectable SOFC performance levels (~400 mW/cm² at 0.7 volts and 800°C) on cells with an active area of 28 cm². A final important outcome of Phase II was the establishment of laser dilatometry and optical profilometry (at Ohio State) as a non-destructive evaluation tool to assess curvature evolution during various stages of the cell manufacturing process.

PHASE I: MANUFACTURING COST ANALYSIS AND RISK ASSESSMENT

Phase I Overview

Five manufacturing approaches (or tracks) were considered for producing low-cost, 5-kilowatt solid oxide fuel cell stacks, shown in Table 1. The NexTech and ORNL tracks were pre-selected for development in the project, whereas the UMR and AMI tracks were evaluated as options, with one of these tracks being selected for development in subsequent phases of the program. For each of the approaches, the track leader completed a survey with all of the relevant information required for cost estimation and risk assessment. In addition, the track leaders completed a development plan to culminate in prototype production of fuel cell elements. A sub-group, consisting of process-neutral team members, was tasked with estimating the costs and risks associated with the five approaches.

Cost, volume and weight estimates for each of the five approaches are summarized in Table 2. Based on this analysis, the tape cast and co-extruded planar approaches all have projected stack costs of \$139 to \$150/kW. In this cost range, it is predicted that the \$400/kW target for total fuel cell system cost could be recognized. The highest production cost (\$179/kW) was predicted for the ultra-thin electrolyte approach. This high cost is due to the assumption of a lower power density (which may be offset by a lower operating temperature). The proprietary cell design was estimated to have the lowest cost because of very high materials utilization. The materials costs are significantly reduced due to the high volumetric efficiency associated with this design. All of the approaches, if successfully developed, represent significant improvements to the state-of-the-art of solid oxide fuel cell manufacturing technology.

Table 1. Description of manufacturing approaches and designs		
Approach	Description	Track Leader
Cathode-Supported Cell	Planar fuel cell with tape cast and co-sintered elements	NexTech Materials
Anode-Supported Cell	Planar fuel cell with tape cast and co-sintered elements	Oak Ridge National Laboratory
Cathode-Supported Cell	Planar fuel cell with ultra-thin electrolyte layers	University of Missouri-Rolla
Anode-Supported Cell	Planar fuel cell with co-extruded and co-sintered elements	Adaptive Materials
Proprietary Cell A	Co-extruded proprietary design	None

An assessment of risks associated with each of the approaches was made using an Analytical Hierarchy System method. The neutral sub-group members reviewed track member input and ranked each approach according to fifteen risk factors. Results of the assessment are summarized in Table 2. Based on this assessment, the lowest overall development risk was predicted for the cathode-supported (NexTech and UMR) approaches, while AMI's co-extruded approach had the highest risk. Risks associated with sealing and manifolding were lowest for the NexTech and ORNL approaches and highest for the AMI and UMR approaches. The risk assessment team was able to rank various approaches – however, the assessed risk differences between the various approaches were fairly small. Based on cost and risk assessment results, the optional UMR track was selected for parallel development in subsequent phases of the program.

Table 2. Summary of cost estimation and risk assessment results					
Configuration	Stack Cost (\$/kW)	Volume (kW/liter)	Weight (kg/kW)	Overall Risk (*)	Sealing Risk (*)
NexTech Cathode Supported Cell	139	0.47	7.18	1	1
ORNL Anode Supported Cell	150	0.47	7.21	4	2
UMR Cathode Supported Cell	179	0.38	8.98	2	4
AMI Anode Supported Cell	145	0.47	7.22	5	4
Proprietary Cell A	94	1.20	1.92	3	3
(*) Risk rankings based on following scale: 1 = lowest risk, 5 = highest risk					

Phase I Methodologies

Methodologies for characterizing the relative costs and risks associated with each of the approaches were based on well-established practices. A sub-group of the MLFCA team was established to perform the cost and risk assessments. The group consisted of Mike Cobb and Kirby Meacham of MAC&Co, Jim Stephan of AMT, and Bob Remick of GTI. These team members have unique experience in design and cost estimation, engineering and manufacturing, and fuel cell technology, respectively. The team members were chosen based on this experience and the fact that they are neutral to the selection of any one technology or path over another. A survey was prepared by the sub-group to solicit required information from each of the developers. In addition, the developers were tasked to complete a development plan to help the group assess development risk. The individual plans were submitted under separate cover as part of NexTech's Management Plan. Track leaders were consulted when technical questions arose but did not participate in the assessment process – to maintain impartiality.

Cost Estimation Approach

The methodology used for estimating manufacturing costs for the various cell and stack designs is outlined by the flowchart in Figure 1. These manufacturing cost estimates were based on three major inputs:

- 5-kW stack designs that define the component geometry in enough detail to calculate the material content and the areas that must be processed.
- Manufacturing plans that define the processes, manpower and equipment to manufacture and assemble the components at a volume of 400 MW/year.
- Operating cost of a Columbus, Ohio based manufacturing plant that includes indirect labor, utilities, maintenance, depreciation and cost of capital.

Direct costs are based on estimates of material and factory floor labor costs. The material cost component was built up as follows.

- Pro forma stack designs were made using AutoCad Mechanical Desktop 4.0 (see Figure 2).
- Finished part volumes were calculated. Spreadsheet calculations were used for simple shapes, and AutoCad solid model data were used for more complex shapes.
- Material cost per kilogram and density were determined for each component. Cost and density for standard materials such as metal alloys were obtained from vendors. Data for custom materials such as ceramics were calculated from raw material properties and material formulations. Costs of fugitive binders and other materials that do not end up in the finished product are included.
- Theoretical material costs of each part were calculated from the volume, density and cost data. A process waste factor is then applied to each part to account for trim losses and the like to obtain an actual material cost per part. Similarly, the scrap factor developed in the labor and process analysis is applied to reflect the fact that extra parts must be started to compensate for parts that are broken or out of specification.

Direct labor costs were built up as follows:

- The process steps to produce and assemble the components were determined. The scrap rate for each process was estimated to determine the actual number of parts that must be processed at each step to produce 400 MW/year of stacks. As indicated above, the scrap data are also used to adjust the material estimates.
- Equipment was identified to carry out each process step at the required rate. Generally, a three-shift operation was assumed for continuous processes with high equipment cost such as sintering and tape casting. Approximate equipment costs and floor space requirements were developed as inputs to the overhead calculations.
- Direct labor to carry out the processes over the required number of shifts was estimated based on reasonable manning assumptions and an appropriate level of tooling and automation. A manufacturing run time factor of 85% was used to reflect lunch and break times and machine downtime for repairs and maintenance.
- Direct labor rates were based on statistical data for the Columbus, Ohio area. A benefit factor of 1.4 was used to obtain total annual salary cost.

Figure 1. Methodologies used for estimating cell and stack manufacturing costs.

Figure 2. Pro-forma stack design used by MAC& Co. for estimating planar SOFC stack costs.

- Indirect costs include depreciation, indirect labor and general expenses of doing business. Depreciation was estimated as follows.
- Physical assets including buildings, manufacturing equipment and office and data processing equipment were listed with costs.
- Depreciation schedules were selected according to the type of asset and the applicable tax rules or accounting conventions. Special attention was given to kiln furniture, which is costly and has a life on the order of one year.

Indirect labor costs were built up as follows:

- Numbers of indirect workers were estimated according to job category. Categories included factory floor supervision, quality control, material handling, maintenance, and general management (including secretarial and clerical). Sales, marketing and R&D functions are not included in the manufacturing cost.
- Indirect labor rates were based on statistical data for the Columbus, Ohio area. A benefit factor of 1.4 was used to obtain total annual salary cost.
- Other general expenses of doing business including supplies, taxes, utilities and miscellaneous services, were estimated using generally accepted ratios and professional judgment. Costs for each element were estimated based on the Columbus, Ohio location.
- Cost of capital was estimated based on the current value of capital assets, including land and buildings, equipment, inventory and working capital. A 10% interest rate was used.
- The direct, indirect and capital costs were totaled to obtain the annual manufacturing cost. The manufacturing cost per unit is simply the annual manufacturing cost divided by the units.

Risk Assessment Approach

At the kick-off meeting, risk assessment team members, along with NexTech and ORNL, developed the evaluation criteria for risk assessment to be applied to the approaches under consideration. The evaluation criteria developed at this meeting is listed accordingly:

1. Design Scaleability
2. Possibility of Pinhole-Free Electrolyte
3. Mechanically/Thermally Robust
4. Feasibility has been demonstrated
5. Probability of Development Success
6. Maturity of Process Technology (proven versus lab)
7. Difficulty in Sealing/Manifolding/Tolerance Control
8. Process Scaleability
9. Cell to Stack Assembly
10. Meets Lifetime Criteria (10,000/40,000 hours)
11. Level of Design Complexity
12. In-Process Inspectability
13. Maintainability $\Rightarrow$ Performance *
14. Start-Up Time
15. Environmental Health and Safety (EHS)

- * Substituted Performance for Maintainability, defined as overall operating characteristics including (efficiency, turndown ratio, internal reforming capability and power density).

The process chosen to evaluate risk was based on the principles of the Analytic Hierarchy Process (AHS). The AHS methodology used to perform this assessment is comprised of three fundamental underlying principles: the principle of constructing hierarchies, the principle of establishing priorities, and the principle of logical consistency.

The hierarchy used for this assessment is constructed as outlined below:

Risk Assessment:	Project Team
Development Approaches:	NexTech (cathode-supported) ORNL (anode-supported) UMR (cathode-supported) AMI (anode-supported) Proprietary (cathode-supported)
Criteria for Assessment:	15 Elements as Stated Above

The assessment of this hierarchy was focused on evaluating the relative importance of each element comprising the evaluation criteria used for assessing risk of the three development approaches. The lowest hierarchy level is comprised of all the elements of the evaluation criteria, which require an analysis for establishing relative importance.

The AHP begins by establishing priorities among the elements of the evaluation criteria hierarchy by synthesizing the technology risk assessment team's judgments to yield an overall set of priorities. The final set of relative priorities forms the basis for assessing the probability of success. In making judgments, paired comparisons are applied to combine logical thinking with a sense of informed experience. Thus, subjective judgments can be quantified and converted to a set of priorities for the decision making process. For making pair wise comparisons, a matrix is developed that offers a framework for consistency. This system allows for additional information through all possible comparisons and for analyzing the sensitivity of overall priorities to changes in judgment.

The technology risk assessment team followed the methodology of AHP to establish priorities through a logical process of analyzing the relationships and preferences among the various elements of the evaluation criteria. The AHP establishes priorities by comparing the relative impact of the elements in pairs, thus establishing relationships of relative importance using a matrix method of analysis. The result of this discrimination process is termed a vector of priority, or of relative importance, for all the elements that comprise the evaluation criteria. Evaluations using the pair wise comparison process are repeated for all the elements by judging the intensity of preference for one element over the other. This logical system of synthesizing the risk assessment team's judgments results in a set of net priority weights for evaluating and weighing the importance of each element of the evaluation criteria. In similar fashion, each weighted element (defined as a property by AHP) is then applied to a matrix of the three development approaches.

The final principle of the AHP also provides logical consistency to establish relationships among elements that are coherent for each level of the hierarchy. In this context, consistency means that similar concepts are grouped according to homogeneity and relevance. In addition, consistency provides that the intensities for judging preferences are based on a particular criterion applied in some logical way. The AHP incorporates both the qualitative and quantitative aspects of thought

processes: the qualitative to define the problem and its hierarchy (in this case, the risk assessment analysis for three fuel cell development approaches using the evaluation criteria), and the quantitative to express judgments and preferences concisely. The risk assessment decision-making process utilizes a logically consistent quantitative system for making sound decisions involving complex development strategies where it is necessary to determine priorities and make tradeoffs.

The initial matrix was set-up to prioritize or rank the importance of the elements of the evaluation criteria. Simple rules have been established for performing the pairwise judgments that ultimately are synthesized into a set of overall priorities. A scale of 1 to 9 is applied to judgments for pairwise comparisons. The application of this scale is defined in Table 3. For the preliminary risk assessment, the elements of the evaluation criteria were processed into a normalized matrix with each element numerically calculated, as shown in Table 4.

It should be noted that the rating for element number 1 - 14.3% (Meets lifetime criteria) versus the rating for number 15 - 1.7% (level of design complexity) is nearly an order of magnitude greater in importance, according to this analysis. The priority factors for all elements of the evaluation criteria were established in the attached matrix work sheet. With each element selected as a criterion for the next level matrix in descending order based on final rating, priorities for the three development approaches were then determined using a 3 x 3 matrix. The vector priorities for each approach were then multiplied by the priority-rating factor for each element of the evaluation criteria to produce a vector of overall priority for each of the approaches.

Table 3. Pairwise Comparison Scale		
Intensity of Importance	Definition	Explanation
1	Equal importance	Two elements contribute equally to the objective.
3	Moderate importance	Experience and judgment slightly favor one element over another.
5	Strong importance	Experience and judgment strongly favor one element over another.
7	Very strong or demonstrated importance	An element is favored very strongly over another; its dominance demonstrated in practice.
9	Extreme importance	The evidence favoring one activity over another is of the highest possible order of affirmation.
2,4,6,8	For compromise between the above values	Use to interpolate a compromise judgment numerically.
Reciprocals of above	If element j is assigned one of the above nonzero numbers compared to element k , then k is calculated as the reciprocal value when compared to j	The AHP mandates this calculation to maintain logical consistency of numerical judgments.

Table 4. Ranking of Evaluation Criteria		
No.	Evaluation Criteria Element	Rating (%)
1	Meets lifetime criteria (10,000-40,000 hours)	14.3
2	Performance	13.6
3	Difficulty in sealing/manifolding/tolerance control	12.8
4	Possibility for pinhole-free electrolyte	12.1
5	Probability of development success	8.4
6	Process scaleability	7.7
7	Mechanically/thermally robust	7.5
8	In-process inspectability	4.8
9	Start-up time	3.5
10	Feasibility has been demonstrated	3.3
11	Maturity of process technology proven (proven versus lab)	3.0
12	Environmental, health and safety	2.9
13	Cell to stack assembly	2.3
14	Design scaleability	2.2
15	Level of design complexity	1.7

Phase I Results and Discussion

The product considered for each of the design approaches is a 5-kW, 42-V module. This specification was chosen on the basis of the utility of this type of unit for auxiliary power units for future transportation applications. The 5-kW size can also be combined with other modules for larger power applications such as those envisioned for Vision 21 power plants. Of course, the power and voltage requirements will change depending on the specific target products. However, the base case looked at here provides a reasonable point of comparison for the four approaches considered. As a starting point for the cost/risk analysis, each of the track leaders provided development plans, describing their cell/stack fabrication approaches. These development plans, summarized below, were provided to DOE in a proprietary appendix submitted with the Phase I Topical Report (October 23, 2000).

Co-Sintered Planar Thin-Film Electrolyte Elements (NexTech and ORNL)

Work within this track focused on the development of low-cost ceramic fabrication methods for high-performance tri-layer electrolyte elements with low operating temperatures (700 to 750°C). Specifically, ceramic fabrication methods (tape casting, colloidal spray deposition, and screen printing) were developed to make thin-film electrolyte membranes supported by porous cathode (LSM) or porous anode (Ni/YSZ) substrates. NexTech's initial focus was on cathode-supported configurations, with later work on anode-supported cells (both in collaboration with ORNL and separately). Development approaches that were pursued during Phases II and III are described in Table 5, and outlined below.

Table 5. Advantages of Development Approaches	
NexTech Approach	Rationale and Advantages of Approach
Objective: Reduce SOFC Operating Temperature to less than 800°C.	
Adapt thin-film electrolyte geometry, using yttrium-stabilized zirconia (YSZ) as the electrolyte material.	This will reduce the electrolyte resistance to negligible levels, thus allowing low-temperature operation.
Modify LSM cathode by adding samarium-doped ceria (SDC) to improve low-temperature performance.	Ceria will improve low-temperature performance by increasing ionic conductivity of the cathode.
Incorporate a thin SDC interlayer film between the LSM cathode and YSZ electrolyte film.	The ceria interlayer will improve catalytic performance at the cathode/electrolyte interface, and will prevent reaction between LSM and YSZ.
Fabricate nickel-based anodes from mixtures of nickel oxide and nanoscale electrolyte (YSZ or SDC) powders.	Low-temperature anode performance will be improved by reducing the particle size of YSZ, or by replacing YSZ by a ceria-based electrolyte.
Objective: Reduce Manufacturing Cost	
Support the YSZ electrolyte film on a porous LSM cathode (instead of a porous anode).	Raw materials costs will be reduced significantly. Also, the LSM-based cathode also has a better expansion match with the YSZ electrolyte material.
Use tape casting, colloidal deposition, and screen-printing, and sintering methods to fabricate the tri-layer electrolyte elements.	These are all low-cost, high-volume manufacturing methods.
Deposit the electrolyte films by colloidal deposition from aqueous coating suspensions. Prepare these suspensions using high-yield synthesis processes.	Competing colloidal deposition processes involve non-aqueous solvents. Aqueous processes are less expensive and pose fewer environmental concerns
A cost model for the fabrication process will be developed and updated as modifications to materials or fabrication methods are made and/or considered.	Real-time cost estimation will foster cost-conscious development and allow cost impact to be considered before changing materials or processes.
Objective: Scale-Up Fabrication Process	
Develop fabrication processes that can be scaled to production of planar tri-layer elements of 100-cm ² areas.	Most planar SOFC developers are targeting the same electrolyte areas for their stacks – thus, it will easier to make comparisons of stack performance.
Support the YSZ electrolyte film on a porous LSM cathode (instead of a porous anode).	Thermal expansion match between the LSM cathode support and the YSZ electrolyte film makes it more feasible to achieve large electrolyte elements.
Evaluate single-cell and long-term SOFC performance at Northwestern and GTI.	Northwestern and GTI, with considerable experience in SOFC testing, will provide independent evaluations of the developed SOFC materials technology.

The successful fabrication of low cost SOFCs that operate efficiently at low temperatures requires an integrated approach to materials selection, design, and fabrication of the electrolyte elements, in concert with stack design, engineering and testing. Cost considerations require the selection of inexpensive materials and fabrication methods, while the low operating temperature requires a thin-film electrolyte configuration. NexTech's manufacturing processes for cathode-supported elements (see Figures 3 and 4) involves the following operations: tape casting porous cathode substrates, depositing electrolyte films from colloidal aqueous suspensions, co-sintering cathode-supported electrolyte films, and deposition of anode coatings by screen printing. With separate funding, ORNL focused on tape casting of porous anode substrates, screen printing of electrolyte films by screen printing, co-sintering of anode/electrolyte bi-layer components, and deposition of anode coatings by screen printing.

To achieve low operating temperature of SOFC elements, optimization of the cathode and anode materials was required. Approaches for optimizing the cathode material include modifying the LSM composition (e.g., Pr substitution for La, Fe for Mn, etc.), incorporating electrolyte material (YSZ or ceria) into the cathode, and incorporating a catalytic ceria interlayer between the LSM cathode and YSZ electrolyte film. Anode optimization approaches pursued included modification of the anode composition (e.g., by substitution of YSZ with ceria), and increasing the level of micro-scale mixing between the YSZ and NiO phases

Figure 3. Fabrication process for cathode-supported, thin-film electrolyte SOFCs.

Figure 4. Schematic of co-sintered cathode/interlayer/electrolyte elements.

Ultra-Thin Electrolyte (University of Missouri–Rolla)

By processing and operating a solid oxide fuel cell (SOFC) at low temperatures ($600\text{-}700^\circ\text{C}$) issues related to interfacial reactions and associated electrical degradation can be circumvented. The UMR approach is based on a planar SOFC configuration using thin film deposition processes in which the processing temperatures never exceed 600°C . Figures 5 and 6 exhibit two views of the Quadrilayer SOFC design: one using a porous cathode as the support substrate (Figure 5), and the other using a porous anode as the support substrate (Figure 6). These designs have the following features in common:

- (1) The porous substrate serves as the building block. The requisite volume fraction and size of the porosity will be dictated by the gas diffusion and associated pressure drop. A graded pore size distribution (i.e. fine-scale porosity) near the interface with the electrolyte will increase the three-phase boundary length, and simplify deposition of the thin films. The substrate will have a thickness dictated by mechanical strength considerations, as well as minimizing the lateral pressure drop. The latter may require a greater thickness, which would not be a problem if the anode were the substrate due to its high conductivity. The porous substrates will be processed using standard tape casting procedures.

- (2) The porous substrate is covered on one side by a dense, thin-film interconnect. The two sides are covered by the dense electrolyte. Currently the interconnect material of choice is based on doped LaCrO_3 , but it is also possible that a dense metallic interconnect could be deposited. The metal may also be oxidized as long as the oxide scale is an electronic conductor. In this design, the thickness of the interconnect layer is not as important as its ability to form a gas tight seal. The interconnect will most likely be deposited first, since its processing temperature to achieve full density is slightly higher than the other components.
- (3) The electrolyte will be a thin film deposited directly onto the porous substrate. A major advantage of this approach is the potential to dope the ZrO_2 with Sc^{3+} instead of Y^{3+} . This results in an improvement in conductivity by over one order of magnitude at 600°C . Since the volume of the electrolyte is small, the higher cost of the scandium raw material becomes insignificant. Note this layer completes the seal on the fourth side, resulting in a structure, which has unidirectional porosity.
- (4) Depending upon whether the porous substrate was the cathode or anode, the next layer deposited onto the electrolyte will be an electrode. If it is the cathode, a thin film of the dense mixed conductor (LSCF) will be used. If it is the anode, then a porous Ni/YSZ cermet will be deposited. In both instances, a SDC buffer layer may be integrated into the design in order to improve the cell performance. This completes the Quadrilayer building block.

Figure 5. Cathode-supported Quadrilayer SOFC element.

Figure 6. Anode-Supported Quadrilayer structure.

- (5) The Quadrilayer building blocks are connected in series by a porous metal structure, which has metal edge runners, which serve as the spacers (Figure 7). The metal composition will depend upon the design. If a porous anode substrate is used, the metal must withstand oxidizing conditions, therefore it would probably be the same composition as the interconnect. When a porous cathode substrate is used this metal must withstand reducing conditions. This is one of the advantages of using a cathode substrate in that it increases the number of possibilities for the metal composition. The porous structure, which provides a path for gas flow, could be a felt, or a corrugated or channeled structure. Note the edge runners are placed orthogonal to substrate sealed edges; this results in a crossflow design. The metal runners serve the additional role of providing a high thermal conductivity path to aid in thermal management of the fuel cell.
- (6) The only place where a glass seal is required is the connection between the metal edge runners and Quadrilayer.

Figure 7. Quadrilayer SOFC module with a porous cathode (a) or anode (b) as the supporting structure.

Co-Extrusion of Electrolyte Elements (Adaptive Materials, Inc.)

MFCX is a thermoplastic powder forming technique that utilizes repetitive passes of a controlled geometry feedrod through a reduction die to achieve very large size reductions. This essence of this novel processing approach is best described through a pictorial example shown in Figure 8. For this example, two thermoplastic compounds were created using alumina and carbon black fugitive powders (white and black phases, respectively). The alumina compound was warm molded into a 40 mm square prism and the fugitive compound into a 25 mm diameter cylinder. The highly filled alumina compound was drilled using standard machine tools and the fugitive cylinder was inserted to create the first feedrod, as pictured in the figure. This feedrod was forced through an 8:1 reduction die in the manner depicted in the cartoon. During co-extrusion the cross section of the extrudate material exiting the die is reduced in size while maintaining the identical cross section as the initial feedrod. Sixty-four sections of extrudate were bundled and assembled together to form the second feedrod (also pictured in the figure). The second feedrod was forced

through the same reduction die as the first. After the second co-extrusion pass the size of the original feedrod design was reduced by a factor of 64 times. Two more co-extrusion passes were completed using feedrods constructed from extrudate created in the previous co-extrusion pass. After the fourth and final co-extrusion pass, the original design was reduced by a factor of 4096 times while the population of fugitive cylinders was increased to over 1,290,000 per square centimeter. The polymer binder was removed from the final part by slowly heating in air to 450°C, the fugitive carbon black was removed by oxidation at 600°C, and the part was sintered at 1600°C for 1 hour. An SEM image of the as fired surface of the final part is shown in the figure, note the regular array of 5-micron cylindrical channels, which run the entire length of the part (in the direction perpendicular to the image).

Figure 8. Pictorial example depicting MCFX fabrication process.

The utility of the MCFX technique for SOFCs is exemplified by the successful fabrication of multi-component and complex ceramic shapes. MFCX has been demonstrated using a wide variety of ceramic (carbides, nitrides, and oxides) and metallic powders. In each case the results were indifferent to the starting powder size or morphology. In addition to geometric flexibility inherent to the MFCX feedrod forming methodology (feedrods are constructed using large-scale thermoplastic forming and/or machining methods), MFCX can deliver several different materials with precise organization and structure. To demonstrate these capabilities, a few example architectures are highlighted in Figure 9. An experimental piezoelectric hydrophone fabricated from PbZrO_3 - PbTiO_3 ceramic is shown in Figure 9a. The target architecture design is included as an inset in the SEM image. The final device has self-supporting ceramic walls only 12 microns thick. An aluminum oxide “reed” structure is shown in Figure 9b. It is a tube with a fine honeycomb lattice enclosed in a cylindrical frame. These honeycomb tubes were coiled or knotted in the green state when the channels were still filled with fugitive and they serve to

illustrate the post-coextrusion shaping capabilities available with MFCX. A metallic nickel topology structure designed to have a negative Poisson's ratio elastic response is shown in Figure 9c. The black and white image inset into the SEM micrograph is the original optimized design. Finally, Figure 9d demonstrates the capability of MFCX to create an intricate two-component architecture, in this case a ceramic-metal composite made with lead magnesium niobate-lead titanate ceramic and silver palladium metal. The image shows that both the ceramic and metal sintered to near theoretical density with well-defined square channels left empty by the fugitive phase. The Ag-Pd metal layers are five microns thick, and the ceramic layers are 15 microns thick.

Fine-scale features can be made using the MFCX, because modules are assembled from centimeter-sized thermoplastic pre-forms (blocks and slabs) into feedrods, which are reduced and reproduced into thousands of micron-sized elements. The final geometry of the co-extruded part can range from thin sheets to large diameter rods. Complex shapes cost no more than simple shapes, because the MFCX method uses piston extrusion with simple tooling (circles, squares, and slabs) to make very complex shaped objects. The key feature is the use of low-cost carbon black fugitive material to define those areas, which after sintering will be empty channels.

Figure 9. Examples of components fabricated by MFCX.

The design of the cathodes, anodes, and electrode/electrolyte interface are known to play a critical role in determining the magnitude of the exchange current density and overpotentials. Three continuous interpenetrating networks must be optimized at the electrode/electrolyte interface to create porosity for gases, electrolyte for oxygen ions and electrode for electrons. It is important to maximize the triple phase boundary (TPB) line length for charge transfer reactions. Features such as fine porosity and finely dispersed YSZ within electrode increase the TPB length, and are desired for decreased overpotential. Simultaneously it is important to limit diffusion polarization effects by not constricting gaseous transport through the porous electrodes. The requirements for the electrolyte, electrode and electrode/electrolyte interfaces involve compromises between the fine-scale structure desired for large TPB and the high permeability desired for gas transport. The flexibility of MFCX can incorporate design features to improve gas transport and exchange current density with few compromises while delivering very thin electrolyte layers (~10 microns).

The MFCX process is differentiated by its unique capability to incorporate novel design features and architectural flexibility not possible with conventional ceramic processing methods. MFCX can be done with any set of powders that can be co-sintered, therefore it can incorporate the many possible anode, electrolyte, and cathode materials systems common to SOFC systems. The ease with which MFCX can manipulate local compositions and configurations makes it possible to realize a wide variety of SOFC component designs ranging from simple planar to complex monolithic architectures. Regardless of the SOFC architecture very thin electrolyte layers and optimized electrodes can be included to enhance both gaseous transport and electronic conduction while maintaining the mechanical integrity of the component. In addition to fabricating planar components, Adaptive Materials also explored the possible advantages of several proprietary designs with novel architectural permutations to enhance the overall performance of solid oxide fuel cells while decreasing their manufacturing cost.

Adaptive Materials conducted a successful first attempt investigation into SOFC component manufacture. The demonstration part shown in Figure 10 is the fractured cross section of an anode-supported tube 700 microns in diameter: the outer wall electrolyte (8 mol% YSZ) was 20 microns thick. The anode (32 vol% Ni - 68 vol% YSZ) was 70 microns thick. This effort was a conservative first attempt aimed at demonstrating the feasibility of MFCX to fabricate components from the materials required for a successful SOFC stack.

Figure 10. SEM micrograph of cross-section of MCFX-fabricated tubular SOFC element comprised of a porous 70-micron thick NiO/YSZ anode and a dense 20-micron thick YSZ electrolyte film.

Results of Cost Estimation

The manufacturing cost estimates are based on three major inputs:

- 5 kW stack designs that define the component geometry in enough detail to calculate the material content and the areas that must be processed.
- Manufacturing plans that define the processes, manpower and equipment to manufacture and assemble the components at a volume of 400 MW/year.
- Overhead cost of a Columbus, Ohio based manufacturing plant that includes indirect labor, utilities, maintenance, depreciation and cost of capital.

The design parameters used for each of the approaches are given in Table 6. Additional details on cell and stack designs used for each of the approaches were provided to DOE in a proprietary appendix submitted with the Phase I Topical Report (October 23, 2000).

Stack costs were calculated for each of the approaches based on 400-MW annual production volume. A comparison of the total stack costs for each of the approaches is given in Table 7, and summarized in Figures 11 and 12. Details of the constituent costs were provided in proprietary appendices that were submitted with the Phase I Topical Report (October 23, 2000). Results are summarized below:

- The three traditional planar designs proposed by NexTech, ORNL and AMI provide similar cost and performance, with stack costs ranging from \$139 to \$150 per kW and volumetric efficiencies of 0.47 kW/liter.

Table 6. Design Parameters for Cost Estimation

Configuration	Stack Output (kW)	Volume of Active Area (liters)	Total Stack Volume (liters)	Weight of Active Area (Kg)	Total Stack Weight (Kg)	Active Stack Area (m ²)	Current Density (ma/cm ²)	Cell Voltage (volts)	Power Density (mW/cm ²)	Cells per Stack
NexTech Cathode Supported Cell	5	3.59	10.84	6.5	36.2	1.0	667	0.75	500	56
ORNL Anode Supported Cell	5	3.59	10.84	6.7	36.4	1.0	667	0.75	500	56
UMR Cathode Supported Cell	4	3.59	10.84	6.5	36.2	1.0	571	0.70	400	56
AMI Anode Supported Cell	5	3.59	10.84	6.7	36.4	1.0	667	0.75	500	56
Proprietary Cell A	5	1.03	4.2	1.8	9.7	1.0	667	0.75	500	56

Table 7. Estimated Stack Costs and Performance Ratios

Configuration	Stack Cost (\$/kW)	Material Cost (\$/kW)	Direct Labor (\$/kW)	Indirect Costs (\$/kW)	Cost of Capital (\$/kW)	kW/ Liter of Active Volume	kW/ Liter of Total Volume	kg/kW of Active Volume	Kg/kW of Total Volume
NexTech Cathode Supported Cell	139	92	14	24	10	1.40	0.47	1.29	7.18
ORNL Anode Supported Cell	150	107	11	23	10	1.40	0.47	1.33	7.21
UMR Cathode Supported Cell	179	119	28	23	9	1.12	0.38	1.61	8.98
AMI Anode Supported Cell	145	106	11	20	8	1.40	0.47	1.34	7.22
Proprietary Cell A	94	50	16	21	8	4.87	1.20	0.36	1.92

Figure 11. Breakdown of stack manufacturing cost by category for the five cell/stack design and manufacturing tracks.

Figure 12. Breakdown of stack manufacturing cost by material type for the five cell/stack design and manufacturing tracks.

- UMR's planar design is more expensive (\$179 per kW) and is less volumetrically efficient (0.38 kW/liter); due primarily to a lower assumed power density (400 versus 500 mW/cm²). Otherwise, the UMR design would have been competitive with the other planar designs. Even with a higher stack cost, the lower operating temperature will lead to savings in balance of plant cost and complexity.
- Materials costs correspond to 66 to 73 percent of total stack costs for the traditional planar designs (NexTech, ORNL, and AMI). For these designs, materials cost was dominated by the metallic components – a substantial cost savings will be obtained upon development of inexpensive high-temperature alloys or by reduction of operating temperature to below 700°C. For UMR's approach, materials cost was 66% of total stack cost, which would have been lower except for the assumption of a lower power density.
- The cost per kilowatt is a strong function of stack size. There is substantial cost associated with non-repeat stack components (endplates, tiebars, power takeoffs, ceramic insulators, etc.). Of these, the endplates are especially expensive (~\$9 to \$20 per kW for each of two plates). By increasing stack size, the cost of these non-repeat units on a per-kW basis is reduced.
- Another approach to reducing stack cost would be to modify designs so that some of the non-repeating metal components (tie-bars, endplates, and load-springs) can be removed from the hot zone. This would allow the use of less expensive metals for these components.
- Cost and performance projections for the proprietary cell design are extremely promising, with a stack cost of \$94 per kW and volumetric efficiency of 1.2 kW/liter. In this case, the materials cost is only about 53 percent of the stack cost.

Results of Risk Assessment

The numerical results of the risk assessment are presented in Tables 8 and 9, and summarized below:

Technical Risk Associated with Development. A summary of the results for rating the preferences of each approach on relative terms to each other is reflected in Table 8. The outcome of this analysis indicates that the NexTech cathode-supported approach has the least amount of risk, and that the AMI approach has the most risk. It should be noted that the actual differences between the various approaches were minimal, given that a scale of 1 to 9 was used and the normalized score for the NexTech approach was only 1.32. An important consideration when evaluating the results of the risk assessment is that actual rankings are very sensitive to the weighting factors used for the evaluation criteria. In this assessment, 76% of total risk scores were derived from only seven criteria. Thus, analyses of the technical rationale used for comparing individual criteria for the design approaches provide extremely useful information. These rationales are summarized in Table 10.

Technical Risk Associated with Sealing and Manifolding. Sealing and manifolding risk was included in the overall risk factors presented in the previous section. Because this has been identified as a critical issue in SOFC commercial development, we also looked at it as a separate risk factor. A comparison of risk for each of the approaches with regard to sealing and manifolding is given in Table 9. Again, the NexTech cathode-supported planar approach scored highest, and that the AMI and UMR approaches were assessed to be the riskiest.

Table 8. Assessment of Development Risk		
Development Approach	Vector of Overall Priority	Normalized Preference Scaling Factor
NexTech Cathode-Supported	0.227	1.32
ORNL Anode-Supported	0.194	1.12
UMR Ultra-Thin Electrolyte	0.205	1.19
AMI Anode-Supported	0.172	1.00
Proprietary Cell A	0.202	1.17

Table 9. Assessment of Risk Associated with Sealing and Manifolding		
Development Approach	Vector of Priority	Normalized Preference Scaling Factor
NexTech Cathode-Supported	0.31	2.07
ORNL Anode-Supported	0.21	1.40
UMR Ultra-Thin Electrolyte	0.15	1.00
AMI Anode-Supported	0.15	1.00
Proprietary Cell A	0.18	1.20

Table 10. Technical Rationale behind Risk Assessment Results						
Criterion	Assessment Results (*)					Rationale
	NTM	ORNL	AMI	UMR	PCA	
Lifetime	0.0386	0.0193	0.0193	0.0387	0.0387	Cathode-supported designs were ranked higher based on Siemens-Westninghouse life data (~100,000 hours), compared to known data for anode-supported designs (~1000 hours).
Performance	0.0250	0.0250	0.0250	0.0167	0.0375	The UMR design was ranked lower due the assumption of a lower power density (W/cm ²). The proprietary cell design was ranked higher based on its higher volumetric power efficiency (W/cm ³).
Difficulty of Sealing and Manifolding	0.0446	0.0298	0.0223	0.0223	0.0254	The NexTech cathode-supported configuration was ranked highest, because failures of edge seals will cause mixing of air and fuel within the anode chambers (and possible failures due to nickel oxidation). Conversely, failures of the edge seals of a cathode-supported design would not be a major problem. Note that failures of manifold seals would cause problems for both anode and cathode supported designs (i.e., reduction of LSM, or oxidation of nickel). The UMR design was ranked lower, due to a smaller seal area.
Possibility of Achieving Pin-Hole Free Electrolyte Films	0.0160	0.0116	0.0081	0.0286	0.0083	The AMI and proprietary cell designs were ranked lowest because it is more difficult to achieve defect-free electrolyte layers with an extrusion-based process. The ORNL anode-supported design was ranked slightly lower than the NexTech cathode-supported design, because it would be marginally more difficult to achieve defect-free electrolyte films with screen printing compared to colloidal-spray deposition. The UMR design was ranked highest because of the multi-step depositions inherent to the spin-coating process (each spin-coated layer will heal defects in the underlying layer).
Probability of Development Success	0.0191	0.0225	0.0165	0.0165	0.0148	The ORNL anode-supported design was ranked highest, because of success achieved at Global Thermoelectric, ECN, and elsewhere. The AMI and proprietary cell designs (based on co-extrusion) were ranked lowest, due to the need for co-sintering three layers. The UMR design also scored low, due to its need to operate at lower temperatures.

Table 10. Technical Rationale behind Risk Assessment Results (continued)						
Criterion	Assessment Results (*)					Rationale
	NTM	ORNL	AMI	UMR	PCA	
Process Scalability	0.0130	0.0149	0.0231	0.0112	0.0182	The AMI and proprietary cell designs were ranked highest because extrusion was deemed the most scaleable of all fabrication processes, and the UMR design was ranked lowest because the screen-printing process was deemed to be the most capital intensive. The ORNL anode-supported design was ranked higher than the NexTech cathode-supported design, since large-area cells and small stacks have already been demonstrated for competing anode-supported planar designs.
Mechanically and Thermally Robust	0.0195	0.0133	0.0123	0.0195	0.0101	The anode-supported planar (ORNL and AMI) designs were ranked lower than the cathode-supported planar (NexTech and UMR) designs because of issues related to thermal cycling (differential thermal expansion) between the anode substrate and electrolyte film, and due to anticipated problems with the nickel reduction step. The proprietary cell design was ranked lowest due to anticipated issues related to thermal cycling of the integrated manifolds.
In-Process Inspectability	0.0128	0.0087	0.0081	0.0128	0.0067	The anode-supported planar (ORNL and AMI) designs were ranked lower than the cathode-supported planar (NexTech and UMR) designs because a critical step in the process (nickel oxide reduction) occurs after all of the fabrication has been completed. The AMI design was ranked slightly lower than the ORNL design because there would be no easy way to inspect the central layer of the tri-layer elements. The proprietary cell design was ranked lowest because multiple cells are fabricated at the same time, making inspection even more difficult.
Start-Up Time	0.0057	0.0056	0.0051	0.0075	0.0094	The proprietary cell design was ranked highest because this design utilizes less material (per kilowatt), so there is less mass to heat up. A possible start-up related benefit of anode-supported cells is the higher thermal conductivity of the nickel-metal containing anode support – this advantage was mitigated by the thermal expansion mismatch between the anode support and the electrolyte film.

Table 10. Technical Rationale behind Risk Assessment Results (continued)

Criterion	Assessment Results (*)					Rationale
	NTM	ORNL	AMI	UMR	PCA	
Feasibility Demonstrated	0.0070	0.0111	0.0063	0.0054	0.0054	The ORNL anode-supported design was ranked highest because of the cell/stack demonstrations achieved at Global Thermoelectric, ECN, and elsewhere. The two designs (AMI and proprietary cell) based on co-extrusion were ranked lower than the cathode-supported (NexTech and UMR) designs, because the required fabrication and sintering methods have been demonstrated.
Process Maturity	0.0083	0.0091	0.0058	0.0084	0.0060	Essentially the same rationale as described above.
Environmental Health & Safety	0.0049	0.0095	0.0062	0.0049	0.0062	The ORNL anode-supported design scored highest because aqueous tape casting will be used for the support electrode (i.e., the largest volume component in the cell).
Cell-to-Stack Assembly	0.0046	0.0046	0.0046	0.0046	0.0061	The proprietary cell design requires less assembly, because multiple cells are fabricated within a single building block (with built-in manifolds). The other planar designs all are internally manifolded, which makes assembly easier.
Design Scalability	0.0043	0.0043	0.0054	0.0043	0.0054	The AMI and proprietary cell designs were ranked highest because extrusion was deemed the most scaleable of all fabrication processes.
Level of Complexity	0.0040	0.0040	0.0040	0.0040	0.0040	The assessment team found no way of differentiating the five designs based on this criterion.
(*) The assessment results are the “vectors of overall priority”, as described in Risk Assessment section of the Phase I report. Acronyms used for the individual designs are as follows: <ul style="list-style-type: none"> • NTM: NexTech co-sintered, cathode-supported planar • ORNL: Oak Ridge co-sintered, anode-supported planar • AMI: Adaptive Materials anode-supported, co-extruded planar • UMR: University of Missouri-Rolla ultra-thin, spin-coated electrolyte • PCA: Proprietary Cell A (co-extruded) 						

Phase I Conclusions

Manufacturing costs were estimated for five-kilowatt stacks based on five development approaches (or tracks):

- Cathode-supported, co-sintered planar design (NexTech, baseline development track)
- Anode-supported, co-sintered planar design (ORNL, baseline development track)
- Anode-supported, co-extruded and co-sintered design (AMI, optional development track)
- Cathode-supported, ultra-thin electrolyte design (UMR, optional development track)
- Proprietary cell design (for comparison only)

The estimated stack costs ranged from \$139 to \$179 per kW for the planar SOFC stacks and \$94 per kilowatt for an SOFC stack based on the advanced design. Conclusions from the cost analysis are summarized below:

- For all SOFC designs, stack costs are very dependent on power density and operating temperature. The key to achieving stack costs of less than \$100 per kilowatt will be to achieve power densities of at least 500 mw/cm² of active area, and to reduce operating temperature to less than 700°C. For the planar designs, materials costs corresponded to 66 to 73 percent of total stack costs and were dominated by the metallic components – a substantial cost savings will be obtained by developing inexpensive high-temperature alloys (or by reducing operating temperature).
- Another important cost consideration that was identified is control of the raw material source. For example, the current high-volume cost of the yttrium-stabilized electrolyte material is \$75 per kilogram, whereas NexTech estimated a high-volume cost of \$20-25 per kilogram based on its existing process. A low cost of YSZ is critical to achieving low cost for anode-supported designs.
- There is substantial cost associated with non-repeat stack components (endplates, tiebars, power takeoffs, etc.). By increasing stack size, cost of these non-repeat units on a per-kW basis is reduced. Another approach to reducing cost would be to modify designs so that some of the non-repeating metal components (tie-bars, endplates, and load-springs) can be removed from the hot zone. This would allow the use of less expensive metals.
- Cost and performance projections for the proprietary cell design are extremely promising, with a stack cost of \$94 per kW and volumetric efficiency of 1.2 kW/liter. For this design, cost and volumetric efficiency are greatly improved due to very high materials utilization.

A risk analysis was conducted and identified distinct risks for each approach, and identified critical risk areas to be addressed during development. Based on the assessment methodology, the lowest overall development risk was predicted for the cathode-supported (NexTech and UMR) approaches. However, the absolute levels of risk were fairly similar for all of the various approaches.

Based on cost and risk assessment results, the optional UMR track was selected for parallel development (along with the NexTech and ORNL approaches) in subsequent phases of the project.

PHASE II: DEVELOPMENT OF SOFC MANUFACTURING PROCESSES

Phase II Overview

Based on the results of Phase, three design/fabrication approaches (or tracks) for planar SOFC elements were selected for development in Phase II and testing in Phase III. These included the baseline tracks (led by NexTech and ORNL) and the Option 1 track (led by UMR). The focus of Phase II was on development and scale-up of the fabrication methods used to make the planar cells. The unit operations involved in SOFC fabrication for the three development tracks pursued in Phase II are shown in Figure 13. Technical challenges addressed by work in Phase II are summarized in Table 11. The work in Phase II was highly collaborative, with NexTech and UMR working together on cathode substrate fabrication, NexTech and Ohio State working together on co-sintering processes, and NexTech and ORNL collaborating on screen-printing processes. Results obtained at NexTech, ORNL, and UMR are described separately, below.

Figure 13a. Unit operations required for fabrication of planar SOFC elements using the process developed by NexTech (Track 1).

Figure 13b. Unit operations required for fabrication of planar SOFC elements using the process developed by ORNL (Track 2).

Figure 13c. Unit operations required for fabrication of planar SOFC elements using the process developed by UMR (Track 3).

Table 11. Technical Challenges and Development Approaches	
Primary Technical Challenges	Development Approaches
Track 1. Cathode-supported SOFCs with colloidally deposited YSZ electrolyte films (NexTech)	
Fabrication of porous LSM substrates with controlled porosity and sintering shrinkage.	Optimization of particle size and surface area of LSM powder; addition of pore-forming fugitive organic particles to control pore size.
Co-sintering of bi-layer LSM/YSZ electrolyte elements with minimal warping.	Optimization of lamination and binder burnout conditions, use of constrained sintering methods.
Prevention of adverse chemical reactions between LSM and YSZ during co-sintering.	Incorporation of a ceria-based interlayer between the LSM substrate and deposited YSZ films.
Achieving high-density YSZ electrolyte films with relatively low sintering temperatures.	Colloidal-spray deposition using an engineered YSZ coating suspension based on nanoscale materials technology.
Scale-up of electrolyte coating process to large element areas.	Adaptation of coating suspensions for use with a continuous ultrasonic spray deposition system.
Achieving high performance in SOFCs operating at low temperatures.	Development of nano-composite cathode and anode materials using nanoscale materials technology.
Track 2. Anode-supported SOFCs with screen-printed YSZ electrolyte films (ORNL)	
Fabrication of porous NiO/YSZ substrates with controlled porosity and sintering shrinkage.	Optimization of particle size of nickel oxide and YSZ powders; addition of pore-forming fugitive organic particles to control pore size.
Co-sintering of bi-layer anode/YSZ electrolyte elements with minimal warping.	Optimization of lamination and binder burnout conditions, use of constrained sintering methods.
Deposition of high-quality YSZ electrolyte films that can be sintered to high density	Screen-printing of YSZ films using a specially developed ink formulation.
Scale-up to large electrolyte element areas.	Use of inherently scalable tape casting and screen-printing process for element manufacture.
Track 3. Cathode-supported SOFCs with spin-coated YSZ electrolyte films (UMR)	
Fabrication of porous LSM substrates with controlled porosity.	Optimization of particle size and surface area of LSM powder; addition of pore-forming fugitive organic particles to control pore size.
Deposition of ultra-thin and dense YSZ electrolyte films on porous substrates by spin coating.	Deposition of ceria-based, pore-tightening planarization layer, which is designed to improve low-temperature cathode performance.
Minimization of defects in spin-coated YSZ electrolyte films.	Deposition of films in a clean room.

Phase II Results and Discussion (NexTech, Track 1)

Most of NexTech's work in Phase II focused on development of manufacturing processes for planar SOFC elements by the fabrication process outlined in Figure 13a. Unit operations include: tape casting and lamination of a 1-mm thick support electrode (cathode or anode); colloidal spray deposition of a 10-micron thick YSZ electrolyte film; co-sintering of the bi-layer element; and screen-printing of the opposite electrode (anode or cathode). Most of NexTech's effort focused on cathode-supported cells, although the developed processes were successfully adapted to the fabrication of anode-supported elements later in Phase II.

LSM Powder Production

Most of NexTech's work in Phase II was focused on the development of fabrication processes for cathode-supported elements. This required relatively large quantities of LSM powder that was engineered for the tape casting process used to fabricate cathode substrates. NexTech's strategy was to produce an LSM powder that sintered to high density in the temperature range of 1300 to 1350°C, where co-sintering with subsequently deposited YSZ electrolyte coatings was to be performed. A low-cost powder preparation process based on ball milling and calcination of lanthanum, strontium and manganese carbonates. Single-phase LSM powder was formed upon calcination at 1000°C, as shown by the x-ray diffraction pattern shown in Figure 14. Attrition milling and vibratory milling methods were used to reduce particle size and increase surface area of calcined LSM powder. Sintering studies were performed on isostatically pressed discs and it was found that LSM powder with a surface area of 7-8 m²/gram provided the desired sintering performance (i.e., full densification at ~1300°C). A particle size distribution curve for LSM powder produced by the optimized milling and calcination methods is shown in Figure 15, which is consistent with a 1-2 micron particle size. NexTech also verified that sintered LSM ceramics produced from this powder exhibited high electrical conductivity (see Figure 16). These conductivity data are consistent with results found in the literature. NexTech's LSM powder process was scaled to the production of up to ten kilograms per week, which met the needs of NexTech's development work in Track 1 and collaborative work with UMR in Track 3.

Fabrication of LSM Cathode Substrates

Development of tape casting and sintering processes for production of porous LSM substrates in Phase II supported both NexTech's development work in Track 1 and UMR's work in Track 3. The targeted process would produce cathode substrates with controlled shrinkage (~20%) during sintering and optimum porosity (40 vol%) after sintering. One of NexTech's strategies in substrate manufacture was optimization of the microstructure of sintered LSM substrates – to minimize the volume of fine-scale porosity (to maximize gas flow during SOFC operation) and to maximize the density of the LSM skeletal structure (to increase mechanical integrity of the substrates). In general, process development involved identifying a suitable solvent/binder system for tape casting of uniform green LSM sheets (100 to 150 microns thick), with fugitive organic pore-forming particles (e.g., starches and polypropylene) added to the slurries prior to tape casting. After tape casting, individual tapes were cut into sections of appropriate size, stacked to form a substrate of desired thickness (1-2 mm), and laminated in a die by applying moderate pressure (~100 psi) at relatively low temperature (70 to 80°C). Removal of binders and fugitives was achieved by slow heating to a maximum temperature of 600°C. The LSM substrates then were sintered at 1350°C and density and microstructures were evaluated.

Figure 14. X-ray diffraction pattern of phase-pure lanthanum strontium manganite powder.

Figure 15. Particle size distribution of LSM powder.

Figure 16. Arrhenius plots of electrical conductivity versus temperature (four-point method) for various perovskite cathode materials produced during Phase II.

During initial process development, significant curvature was noted in sintered LSM substrates; parametric studies were performed to address this problem. For these studies, curvature of sintered LSM substrates was assessed by optical profilometry at Ohio State University. As shown in Figure 17, two types of curvature were observed, depending on the orientation of tape layers during lamination. A “saddle-type” curvature (Figure 17a) was observed when tapes were laminated with random orientation (relative to the tape casting direction), whereas a “one-way” curvature (Figure 17b) occurred when orientation of tapes was maintained. It is believed that this curvature is caused by non-uniform green density of LSM tapes due to binder segregation during drying of cast tapes. This curvature was eliminated the component steps in LSM substrate manufacture were optimized (see Figure 18). The microstructure of a sintered LSM substrate produced by the optimized process is shown in Figure 19. The high-density “skeletal” LSM structure was obtained, which was one of our process development targets. Important process steps related to LSM substrate fabrication are discussed below:

- Lamination conditions were established through an iterative process between optimizing tape casting formulations and lamination conditions to achieve optimum uniformity and minimal green density variations. Incorporation of a stress relaxation step (i.e., annealing at slightly elevated temperature) after lamination also led to significant reductions of curvature.

Figure 17a. Optical profilometry scan showing “saddle-type” curvature in sintered LSM laminates, with non-optimized processing conditions.

Figure 17b. Optical profilometry scan showing “one-way” curvature in sintered LSM laminates, with non-optimized processing conditions.

Figure 18. Optical profilometry of sintered LSM substrate prepared with optimized processing conditions (note total curvature of 15 microns over 2-cm length).

Figure 19. SEM micrograph of polished surface of porous LSM substrate prepared using optimized process and sintered at 1350°C.

- The different fugitive organic materials used as pore formers affected shrinkage, curvature and microstructure development during sintering. Some of the starch materials evaluated were sensitive to moisture – by working with vendors, a moisture insensitive maltodextrin material was identified that worked best with the tape casting and lamination process.
- Optimization of the binder removal step, which is made more challenging because of the high fraction of organic material (binders and fugitives) in the tape laminates, also was found to be critical for minimizing curvature. Precise control of the heat treatment cycle and thermal uniformity of the furnace were critical for a successful binder burnout process.

Interlayer Material Selection

One of the primary materials issues associated with the cathode-supported SOFC configuration is that LSM and YSZ are known to react at temperatures required for co-sintering of the LSM substrate and YSZ film. An interlayer strategy was adopted to address this reactivity issue and also to improve cathode performance. It is known from the literature that ceria-based electrolytes do not react with LSM, and that low-temperature cathode performance is enhanced when ceria is present at the cathode/electrolyte interface. Thus, gadolinium-doped ceria (GDC) was selected as a component of a composite interlayer. The second component of the interlayer should be a conducting perovskite electrode material that does not react with YSZ during sintering. Based on a review of the literature, we evaluated several perovskite compositions in the praseodymium strontium manganese iron oxide (PSMF) system. Ceramic powders of the candidate PSMF compositions were prepared by milling and calcination methods. Single-phase perovskite PSMF powders were prepared, as shown by the x-ray diffraction pattern in Figure 20. Dense ceramic samples also were prepared from the PSMF powders, and electrical conductivity measurements were made by the four-point method. LSM and PSMF powders were hand-mixed with YSZ, GDC, and Sm-doped ceria (SDC) electrolyte powders, and pellets prepared from these powder mixtures were then sintered at 1300 to 1400°C for eight hours. X-ray diffraction was used to determine whether any reactions occurred with the electrolyte materials. The results are summarized in Table 12, and below:

- In general, the conductivities of the PSMF ceramics were lower than that of LSM, especially as strontium and iron contents were increased (as presented earlier in Figure 16).
- The reaction between LSM and YSZ to form lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$) was confirmed, as shown in Figure 21.
- The non-reactivity of LSM with both SDC and GDC was confirmed, as shown in Figure 22.
- PSMF compositions with high strontium contents exhibited a reaction with YSZ to form strontium zirconate.
- One particular composition, $(\text{Pr}_{0.80}\text{Sr}_{0.20})(\text{Mn}_{0.50}\text{Fe}_{0.50})$ or PSMF-8255, was selected for the composite interlayer because it did not react with YSZ, SDC or GDC, (see Figure 23 and 24) and had a relatively high electrical conductivity compared to other PSMF compositions.

Table 12. Results of Reaction Studies				
Material	Composition	Reaction Products Observed		
		YSZ	SDC	GDC
LSM	$(\text{La}_{0.85}\text{Sr}_{0.15})\text{O}_3$	$\text{La}_2\text{Zr}_2\text{O}_7$	none	none
PSM-20	$(\text{Pr}_{0.80}\text{Sr}_{0.20})\text{MnO}_3$	none	none	n/a
PSM-40	$(\text{Pr}_{0.60}\text{Sr}_{0.40})\text{MnO}_3$	SrZrO_3	none	n/a
PSMF-5555	$(\text{Pr}_{0.50}\text{Sr}_{0.50})(\text{Mn}_{0.50}\text{Fe}_{0.50})\text{O}_3$	SrZrO_3	none	n/a
PSMF-8255	$(\text{Pr}_{0.80}\text{Sr}_{0.20})(\text{Mn}_{0.50}\text{Fe}_{0.50})\text{O}_3$	none	none	none

Figure 20. X-ray diffraction pattern of phase-pure PSMF-8255 powder.

Figure 21. X-ray diffraction pattern of mixture of LSM and YSZ, sintered at 1350°C for eight hours. Note the formation of a lanthanum zirconate phase.

Figure 22. X-ray diffraction pattern of mixture of LSM and GDC, sintered at 1350°C for eight hours. Note that no second phases are formed.

Figure 23. X-ray diffraction pattern of mixture of PSMF and YSZ, sintered at 1350°C for eight hours. Note that no second phases are formed.

Figure 24. X-ray diffraction pattern of mixture of PSMF and GDC, sintered at 1350°C for eight hours. Note that no second phases are formed.

Electrolyte Coating Process Development

The core to NexTech's electrolyte coating technology is its process for producing nanoscale YSZ suspensions, which can be modified to allow high quality films to be deposited by spray coating methods. The nanoscale component of these aqueous coating suspensions allows the deposited YSZ films to be densified at relatively low temperatures – which is essential for any successful attempt at co-sintering to produce cathode-supported electrolyte elements (given the reactive nature of the LSM cathode material, as discussed above). At the onset of Phase II development work, NexTech's synthesis process for producing nanoscale YSZ suspensions was a low-yield and labor-intensive process and the spray-coating method was a hand-spraying operation. Thus, initial coating process development work in Phase II focused on improving the production process for making nanoscale YSZ suspensions (see Figure 25) and adapting the coating suspensions to allow films to be deposited using an automated ultrasonic spray deposition system (see Figure 26). NexTech's new process provides for the direct production of nanoscale YSZ suspensions with high solids content (~40 wt%), so that a time-consuming solvent-evaporation step is no longer required (the original process provided YSZ suspensions with a solids content of ~4 wt%). The use of the ultrasonic spray coating system greatly improved the uniformity and quality of deposited films, especially as substrate areas were increased. Another step-function improvement in film quality was achieved when this coating system was installed within a clean room (see Figure 27), along with other unit operations required for SOFC fabrication (e.g., tape casting, lamination, and screen printing).

Figure 25. Particle size distributions of aqueous nanoscale YSZ suspensions.

Figure 26. Ultrasonic-spray deposition system used for depositing YSZ electrolyte coatings.

Figure 27. NexTech's multilayer ceramic fabrication clean-room facility.

Fabrication of Cathode-Supported Planar Elements

Most of NexTech's Phase II development work was aimed at cathode-supported planar cells. The primary challenge addressed in this work was that sintering shrinkages of the LSM cathode substrate and the deposited YSZ electrolyte films were not perfectly matched. This was further exacerbated by the need for an interlayer to prevent adverse reactions between LSM and YSZ (as discussed above). The targeted electrolyte element architecture consisted of a 1-mm thick macro-porous LSM cathode substrate, a 10-micron thick micro-porous PSMF/GDC composite interlayer, and a 10-micron dense YSZ electrolyte film. Most of the work was performed using 2.5-cm diameter cathode substrates, whereas later work involved larger substrates (up to 10-cm square). Interlayer and electrolyte coatings were deposited after binder burnout and calcination of the LSM substrates. The composition of the PSMF/GDC interlayer varied from 25 to 40 volume percent GDC, and aqueous coating suspensions were prepared from relatively coarse powders (to prevent excessive densification during sintering). YSZ electrolyte coatings were applied by ultrasonic spray deposition from aqueous coating suspensions prepared by NexTech's patent-pending process. The sintering temperature of the YSZ-coated substrates was fixed at 1350°C.

Our process development work was augmented by the use of laser dilatometry at Ohio State, which is a non-contact method for determining sintering shrinkage of net-shape samples (i.e., samples were the LSM substrates used for coating studies and co-sintering trials). Results and implications of laser dilatometry studies are summarized below:

- As mentioned above, the specific fugitive pore formers used for LSM substrate fabrication had a large impact on sintering shrinkage. This is shown in Figure 28, where lateral sintering shrinkages are compared for laminates prepared from identical LSM powders but with maltodextrin and polypropylene pore formers. Initial sintering occurred at lower temperature for LSM laminates prepared with polypropylene; use of these laminates led to severe differential shrinkage problems during co-sintering (because shrinkage of the LSM substrate occurred at lower temperature than the electrolyte film).
- LSM powder preparation methods affected shrinkage behavior of LSM laminates, as shown in Figure 29. Laminates prepared using LSM powder from our original process showed a significant expansion event at a temperature near 1100°C, perhaps caused by incomplete reaction during calcination (which led to defect formation during co-sintering). This problem was addressed by pre-calcining LSM substrates above the temperature where this expansion occurred. Our LSM powder preparation process was modified so that current laminates do not exhibit this expansion anomaly.
- Laser dilatometry also allowed us to examine the shrinkage of YSZ-coated substrates, as shown in Figure 30. Densification of the coating appears to occur at a higher temperature and constrains shrinkage of the LSM substrate during co-sintering. This led to significant curvature of co-sintered bi-layer element, as well as crack formation in the YSZ electrolyte film. The pre-calcination step, described above, allowed us to tailor the shrinkage behavior of the LSM substrate, thus enabling successful co-sintering of bi-layer elements with optimum flatness and coating quality.

Figure 28. Laser dilatometry of LSM laminates during heating to 1300°C. Note that onset of shrinkage occurred at a lower temperature for LSM laminates prepared with polypropylene pore formers.

Figure 29. Laser dilatometry of LSM laminates during heating to 1300°C. Note that laminates prepared using modified LSM powder do not exhibit an expansion anomaly at 1100°C.

Figure 30. Laser dilatometry of uncoated and YSZ-coated LSM laminates during heating to 1300°C. Note that YSZ coating constrains the shrinkage of the LSM laminates.

Development of co-sintering methods required several iterations between substrate fabrication, binder removal and calcination, interlayer and electrolyte coating deposition, and co-sintering trials. The two primary challenges addressed were optimization of flatness of co-sintered electrolyte elements, and improving quality (density and defect density) of sintered YSZ electrolyte films. The impact of the various processing variables is discussed below:

- **LSM Substrate Fabrication.** Optimization of all of the LSM substrate fabrication steps (tape casting, lamination, stress relaxation, and binder burnout) was critical to successful process development. As discussed above, the LSM substrates were pre-calcined prior to coating deposition, so that the sintering shrinkages of the LSM substrate could be matched with the deposited LSMF/GDC interlayer and YSZ electrolyte films.
- **Deposition of Interlayer Coatings.** It was critically important to control the thickness and morphology of the PSMF/GDC interlayer coatings. Excessive densification of the interlayer had to be prevented – otherwise SOFC performance would be compromised. The interlayer thickness also had to be controlled within a window of 10 to 25 microns – thinner coatings would not prevent the YSZ/LSM reaction during co-sintering, and thicker interlayer coatings increase the challenge of co-sintering. The thickness and morphology of the interlayer coatings were controlled by tailoring particle size of the PSMF and GDC components of the coating slurry and precisely monitoring the coat weight during deposition. An SEM micrograph of the surface of an interlayer-coated LSM substrate is shown in Figure 31, and an optical profilometry scan of the surface topography of this coating is shown in Figure 32. The fine-scale porosity of this interlayer coating met our target of 0.5 microns, and the smoothness of the surface was sufficient for deposition of high-quality YSZ electrolyte films.

- **Deposition of YSZ Electrolyte Coatings.** NexTech's colloidal spray deposition process for YSZ electrolyte coatings is based on an aqueous YSZ suspension having a bi-modal particle size distribution. By controlling the relative amounts of coarse and nanoscale components of this suspension, high green density YSZ films can be deposited. The nanoscale component of the suspension allows for high film densities to be achieved at low sintering temperatures. Most of the coating process development work was devoted to optimization of NexTech's process used for preparing nanoscale YSZ suspension and transferring from an aerosol-spray process to an ultrasonic spray process for coating deposition (as discussed above). Some effort also was devoted to optimizing the dispersion state of the coarse YSZ fraction in the coating suspension. This process refinement work was completed early in Phase II, and the coating process was held constant for the remainder of process development work in Phase II
- **Co-Sintering.** The methods used for sintering of electrolyte-coated substrates also were important to our process development work. Specifically, temperature gradients in the sintering furnace were minimized with appropriate kiln furniture, and sintering cycles were designed based on the laser dilatometry results. The developed co-sintering method involved sandwiching the YSZ-coated laminates between solid GDC plates, or between GDC-coated setter tiles – GDC was selected for this purpose because it is completely non-reactive with LSM and YSZ. With the deposition and co-sintering methods established in Phase II, NexTech was able to achieve dense YSZ electrolyte films, with and without interlayers, as shown in Figures 33 and 34. The process was scaled to an element area of 35-cm² (5 x 7 cm) with overall flatness maintained at less than 100 microns, as shown by optical profilometry scans in Figure 35.

Figure 31. SEM micrographs of PSMF/GDC interlayer coating (deposited on an LSM substrate and sintered at 1300°C).

Figure 32. Optical profilometry scan showing surface topography over a 1-mm by 1-mm area of the interlayer coating shown in Figure 31.

Figure 33. As-deposited (left) and sintered (right) films of YSZ on porous LSM substrates.

Figure 34. SEM micrograph of a fractured cross-section of a cathode-supported element. Note the micro-porous PSMF/GDC interlayer and high-density YSZ electrolyte films.

Figure 35. Optical profilometry scans of 2-cm x 3-cm co-sintered cathode-supported SOFC element, indicating total curvature of less than 100 microns across the cell area.

Fabrication of Anode-Supported Planar Elements

The processes described above were applied to the fabrication of anode-supported elements. Initially, NexTech demonstrated their colloidal-spray process for YSZ electrolyte films, by using NiO/YSZ anode substrates fabricated at ORNL. The substrates were processed through binder burnout as specified by ORNL, spray-coated with YSZ and sintered at 1400°C. A dense YSZ film was achieved, as shown by the SEM micrograph in Figure 36. Subsequently, NexTech adapted its tape casting and lamination processes to the fabrication of NiO/YSZ anode substrates. Nickel oxide powder (reagent grade) was first attrition milled to reduce its particle size, and then mixed with YSZ (Tosoh) by ball milling. The nickel content of the anode powder mixture was fixed at 43 volume percent (after reduction of nickel oxide to nickel metal). The NiO/YSZ powder mixture was then mixed with the binder/fugitive/solvent system established for LSM cathode substrates, with appropriate adjustments made to achieve optimum viscosity for tape casting. Tapes were cast and laminated as described above. After binder burnout and a modest calcination treatment, YSZ coatings were applied by ultrasonic spray deposition, and sintered at 1400°C. With limited process optimization, dense YSZ films were achieved as shown by the SEM micrograph in Figure 37.

Figure 36. SEM micrograph of a polished cross-section of an anode-supported element. The NiO/YSZ anode substrate was made at ORNL, the YSZ film was applied by colloidal spray deposition at NexTech, and the bi-layer element was co-sintered at 1400°C.

Figure 37. SEM micrograph of a polished cross-section of an anode-supported element prepared using processes developed at NexTech. Note the extremely high density of the YSZ electrolyte film. Also note that anode porosity is not evident in this micrograph due polymer intrusion into the pores during sample preparation.

Screen Printing Process Development

Anode screen printing inks were developed in collaboration with ORNL. The anode and cathode formulations subjected to ink preparation and screen printing trials are summarized below:

- Conventional anode powder mixtures were prepared by ball milling nickel oxide (reagent grade) and YSZ (Tosoh) powders. In some cases, the nickel oxide powder was first attrition milled to reduce its particle size. The nickel content of the anode powder mixture was fixed at 43 volume percent (after reduction of nickel oxide to nickel metal).
- Nano-composite NiO/YSZ powder mixtures were prepared (as described below) and calcined to achieve surface areas of 10~20 m²/gram.
- Lanthanum strontium ferrite (LSF) cathode powders (20 and 40 mol% Sr) were prepared using conventional milling and calcination methods, and then attrition milled to a surface area of 10 to 15 m²/gram. Gd-doped ceria (GDC) powder was prepared using NexTech's proprietary synthesis process. LSF and GDC powder mixtures (25 to 40 vol% GDC) were made by ball milling of the two components.

The electrode powder mixtures were incorporated into ORNL's proprietary ink vehicle or a commercial ink vehicle (Hereaus) using a three-roll-mill. A fugitive component also was added to the inks, to assure that sufficient porosity was maintained in the electrode coatings after annealing. These inks have high solids content (15 to 25 volume percent), including ceramic and fugitive components – the solids loading being determined experimentally based on viscosity required for optimum screen-printing. The inks were screen-printed onto dense electrolyte discs using patterned screens of 200 and 135 mesh size. Calcination studies and adherence testing was performed on the inks by sintering the printed inks at temperatures ranging between 1100 and 1350°C. All the cathode and anode inks exhibited good adherence at sintering temperatures as low as 1150°C.

Nano-Composite Anode and Cathode Powders

It is well established that electrode performance in solid oxide fuel cells, both at the anode and at the cathode, improves substantially when the components of composite electrodes are intimately mixed. NexTech demonstrated novel processes for achieving such intimate mixtures by utilizing its nanoscale electrolyte materials (YSZ and GDC) in conjunction with nickel oxide (for anodes) and perovskite electrode materials like LSM, LSF, and PSMF (for cathodes). NexTech's process involves mixing the nanoscale electrolyte material with the second component of the composite electrode in such a way that the electrolyte material coats the larger particles of the second component. After this mixing step, the nano-composite electrode material is calcined to achieve a surface area desired for the intended fabrication process (e.g., 5-10 m²/gram for tape casting, or 10-20 m²/gram for screen printing). NexTech's nano-composite electrode synthesis process was demonstrated for NiO/YSZ anode formulations, PSMF/GDC cathode interlayer materials, and screen-printed cathode formulations (LSM/YSZ, LSM/GDC, and LSF/GDC). An example of the concept is shown in Figure 38, by SEM micrographs of a ball-milled NiO/YSZ anode powder mixture with a nano-composite NiO/YSZ anode powder mixture. The conventional ball milling approach leads to a morphology where discrete NiO and YSZ particles are evident; conversely, the nano-composite approach provides a morphology where nickel oxide particles are coated with YSZ. Upon sintering, the nano-composite approach provides a much more intimate mixture of the two phases.

Figure 38. SEM micrographs of NiO/YSZ anode powder mixtures prepared by conventional ball milling (top) and NexTech's nano-composite synthesis method (bottom). Note the nano-composite anode material is comprised of YSZ-coated nickel oxide particles.

Phase II Results and Discussion (ORNL, Track 2)

ORNL's work in Phase II focused on development of manufacturing processes for planar SOFC elements by the fabrication process outlined in Figure 13b. The approach of this project is to develop an anode supported solid oxide fuel cell using low-cost fabrication technologies such as tape casting and screen printing. The anode support was fabricated using tape casting and lamination to achieve a thickness of 1 mm. The electrolyte then was deposited by screen printing, and the anode/electrolyte bi-layer structure was co-sintered to provide the desired porous substrate, dense electrolyte microstructure. Cathodes were deposited by screen printing followed by annealing. In some cases, catalytic interlayers were incorporated, which also were deposited by screen printing. ORNL's development work is summarized below.

Anode Support Development (Organic System)

Tape casting was chosen as the method to fabricate the anode. The main advantage of tape casting is that it is the best way to form large-area, thin, flat ceramic parts that are impossible to press and difficult if not impossible to extrude. The thin sheets are two-dimensional structures and very thin (thin is defined in microns) in the z direction.

The anode layers were fabricated by both an organic and aqueous tape formulations. The organic tape method employed traditional polymer and organic materials for the batch. A tape process was developed that routinely and reproducibly resulted in uniform anode tapes that had a sintering shrinkage of 18.1% (1400°C, two hours, in air). The average difference in shrinkage between different batches of the same formulation was less than $\pm 0.2\%$, indicating good reproducibility in the formulation developed. Figure 39 shows a cross section of the anode after sintering (Figure 39A) and after reduction in H_2 (Figure 39B).

Figure 39. Cross section (fracture surface) of single sintered (1400°C/2 hr. in air) of anode (A) and after reduction in H_2 at 1000°C (B). Insert in (B) shows enlarged view of cross section in which Ni is spherical nodules in a sintered YSZ matrix.

ORNL's organic tape casting system developed is typical of a commercial organic system. One exception to the commercial formulation was made, ORNL used a proprietary plasticizer that is less hazardous and burns out cleaner than the typical commercial phthalate based plasticizers. The anode tape was blanked by stamping process and laminated to have a thickness just over 1 mm by a modified uniaxial lamination process. The cast tape can be stored for future use after casting, blanking, or lamination for future use.

Anode Support Development (Aqueous System)

A tape casting process was developed that was similar to the organic based process, except the organic vehicle was replaced by water. This process had to be developed to overcome the catalytic nature of NiO. That is, NiO readily reacts with the aqueous binders resulting in either coagulation or crosslinking of the binder. ONRL developed a proprietary tape casting system, which included novel binders and an additive that prevents the catalysis of the binder. This additive is unique and only a few parts per million are required to prevent reaction between NiO and the binders.

As previously described the tapes were blanked and laminated by a uniaxial process. The aqueous tapes have a reproducible sintering shrinkage of 21%. This is higher than the organic shrinkage and indicates the aqueous tapes have a higher green density, better packing, and possible better dispersion than the organic tapes. Figure 40 shows the cross section of a typical aqueous tape after sintering. This system is not fully optimized and requires additional development to increase the amount of porosity and decrease shrinkage to an acceptable level. This was the first demonstration of aqueous tape casting of Ni/YSZ anode materials for any application and the first demonstration that the unwanted catalytic reaction between NiO and organic binders can be simply mitigated.

Figure 40. Cross section (fracture surface) of an anode tape derived from an aqueous binder formulation, sintered in air at 1400°C for two hours.

Screen Printing Development (Electrolyte)

Initial screen printing development took place using a commercially available organic vehicle. This vehicle was mixed with Tosoh 8YSZ powder and printable inks were developed. Inks developed with this vehicle were printed using available screens and sintered to full density with thickness ranging from 9 to 25 μm . A typical micrograph of a fracture surface of one such sample is shown in Figure 41. It is important to note that the electrolyte while being dense still has a large number of pores visible in the cross section. This may be due to the low solids loading achievable with the commercial vehicle. During the course of this development activity, our supplier of vehicle decided not to supply vehicle to the commercial market, opting to develop all inks for customers for a fee. This was not cost effective for this program and therefore, other options were considered.

It is important to note that most commercial vehicles developed to date were developed to blend with noble metals (Pt, Pd) to be used as high-temperature electrode inks. Most, if not all, of these vehicles are incompatible with ceramic (oxide) materials. Therefore, additional vehicles were screened to evaluate their compatibility with YSZ and to see if printable and sinterable inks could be developed. In an effort to use commercially available vehicles a survey was carried out to identify other vehicles produced by the major commercial developers (Ferro, Heraeus, and ESL). In all instances, the suppliers realized the potential of the fuel cell market and were reluctant to share developmental and commercial vehicle systems. Ferro and ESL wanted a fee to develop the inks and the turn around time for this development process became prohibitive. Heraeus evaluated samples of a variety of 8YSZ powders with their vehicles and found that those produced by Tosoh (which were used in this effort) caused their binders to gel. As a result of this study, ORNL decided to develop their own screen printing binder system.

Figure 41. Cross section of screen printed YSZ electrolyte film on an anode substrate, sintered at 1400°C, showing coherent 9 μm electrolyte layer (A); and high magnification of electrolyte showing residual porosity in the electrolyte (B).

Over the course of ten working days ORNL developed a novel screen printing vehicle that is compatible with the electrolyte, cathode, and a variety of other potential SOFC materials. This vehicle facilitated a 20% increase in solids loading of the YSZ electrolyte and resulted in higher green densities in the printed films. A patent has been applied for this binder system. Figure 42 shows typical sintered cross sections of electrolytes deposited using this new organic vehicle system. Figure 42B shows a high magnification of the electrolyte, which indicates that the electrolyte is dense and pores are smaller than those using commercial vehicles. Figure 42C shows a cross section of the microstructure after reduction in H_2 at $1000^\circ C$. The interconnected YSZ backbone and the distinct nickel particles are evident. This screen printing system was used in combination with the anode tape to produce a variety of samples of differing sizes to test the reproducibility and sintering shrinkage of the combined system. Initial samples showed some warping, which was eliminated by adjusting the ink formulation so that shrinkage of the electrolyte film more closely matched that of the anode. Several samples up to 100 cm^2 were produced using this process. Figure 43 shows a 40-mm diameter disk with a green (unsintered) electrolyte (left) and a fully densified electrolyte (right).

Figure 42. SEM micrographs of a cross section of screen printed YSZ electrolyte film on anode substrate, sintered at $1400^\circ C$ for two hours: (a) low-magnification image showing coherent electrolyte layer; (b) high magnification image showing residual porosity in electrolyte film; and (c) image of the bi-layer sample after reduction in hydrogen at $1000^\circ C$. ORNL's proprietary screen printing vehicle used for the preparation of the electrolyte ink.

Figure 43. 40-mm diameter anode with screen printed YSZ layer (left) and similar sample after densification at 1400°C.

Screen Printing Development (Catalytic Layers)

Interfacial layers were developed for both the anode and cathode side of the electrolyte film. These layers were applied by screen printing. The anode catalytic layer was a modified anode composition in which the pore former was modified to give a fine dispersion of interconnected porosity at the anode/electrolyte interface. The anode ink formulation and screens were designed to provide 10- μm thick layer when sintered (see Figure 44). The cathode interfacial layer was screen printed gadolinium-doped ceria, derived from nanoscale GDC powder prepared by NexTech with a surface area of 100 m^2/gm . An ink formulation was developed and printed that resulted in a continuous, partially porous layer of ceria with a thickness of 2 μm (Figure 45). Because this was a nanoscale ceria material, care was taken during sintering to avoid inter-diffusion of ceria into the YSZ electrolyte.

Process Flow Diagram

A flow diagram that describes the fabrication process was developed and is shown in Figure 46. This diagram completely describes all the steps necessary for fabrication of anode-supported SOFCs using tape casting and screen printing methods. The dashed lines in Figure 46 represent optional paths that can be pursued depending on the degree of development required. This diagram only represents the fabrication of the anode/electrolyte bi-layer structure. A subsequent step is required for cathode deposition.

Figure 44. Cross section of fuel cell showing anode, anode catalytic layer, electrolyte, and cathode interfacial layer. All the layers were deposited by screen printing except for the anode, which was prepared by tape casting and lamination.

Figure 45. SEM micrograph of screen printed and sintered ceria interlayer on YSZ electrolyte.

Figure 46. Process flow diagram for solid oxide fuel cells derived from a multilayer ceramic process. (Note dashed lines indicated optional process paths).

Phase II Results and Discussion (UMR, Track 3)

ORNL's work in Phase II focused on manufacturing processes for cathode-supported SOFCs with ultra-thin electrolyte layers, by the fabrication process shown in Figure 13c. The primary challenge addressed in Phase II was the fabrication of cathode substrates with sufficiently smooth surfaces for compatibility with their spin-coating process for electrolyte deposition. Tape casting methods were used to fabricate individual tapes with different pore sizes, and these tapes then were laminated and sintered to achieve a graded-pore cathode substrate. Specific results are described below:

Porous LSM Cathode Substrate Preparation

For UMR's design, the cathode substrate must provide mechanical support for subsequently deposited layers and sufficient porosity to provide gas diffusion to the electrolyte. This type of substrate was developed as follows:

- **LSM Powder Characterization (see Figure 47).** NexTech supplied cathode powder of the composition, $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (LSM), with a surface area of $10 \text{ m}^2/\text{gram}$. SEM micrographs confirmed a particle size of $\sim 0.5 \mu\text{m}$. X-ray diffraction pattern of LSM powder indicated the expected perovskite structure, which was unchanged after sintering at 1450°C for two hours.
- **Fugitive Powder.** Several carbon powders were characterized by SEM and BET surface area analyses. SEM results are shown in Figure 48. The grade 4104 graphite powder offered by Asbury Graphite Mills Inc. was used for initial tape casting and substrate fabrication trials, although a number of others also were evaluated.
- **Tape Casting and Lamination.** The LSM and two Asbury carbon powders were dispersed with fish oil in mixed solvent of ethanol and toluene. The optimum concentration of fish oil was $1.6 \text{ mg}/\text{m}^2$ for the LSM powder and $0.8 \text{ mg}/\text{m}^2$ for carbon powder, respectively. The LSM powder, with or without carbon powder, was mixed with fish oil, binder and plasticizer in ethanol and toluene, then ball milled for two days. The slurries were cast to 125-micron thick tapes. Tapes were laminated at 80°C and 250 psi to obtain 5-cm by 5-cm laminates for sintering trials.
- **Sintering and Microstructural Studies.** The laminates of LSM with and without carbon powder were sintered at various temperatures for two hours. The density as a function of sintering temperature is plotted in Figure 49. LSM tapes prepared without carbon fugitives were sintered to full density at 1350°C for two hours. LSM tapes with carbon fugitives exhibited about 20 volume percent porosity under the same sintering conditions. The microstructure development of LSM without carbon fugitive shows in Figure 50. The average grain size increases with sintering temperature. The fully dense LSM ceramic (sintered at 1350°C) had a relatively small average grain size ($\sim 3.5 \mu\text{m}$), which was desired based on mechanical strength considerations. Based on these results, porous LSM substrates were sintered at 1350°C and 1320°C to obtain high porosity and good mechanical strength. Their SEM photographs, shown in Figure 51, indicate that LSM skeleton is quite dense at the sintering temperatures. The dense skeleton will offer strong mechanical strength.

Figure 47. Characterization of NexTech-supplied LSM powder.

Figure 48. SEM characterization of carbon fugitive powders.

Figure 49. Density versus sintering temperature for LSM substrates

Figure 50. SEM micrographs of sintered LSM tapes, without carbon fugitive.

Figure 51. SEM micrographs of sintered LSM tapes, with carbon fugitive.

LSM Layers with Fine-Scale Porosity

The microstructure and pore size distribution of LSM single layers with fine carbon fugitive were studied as a function of sintering temperature. The results are summarized below:

- **Pore size distribution.** The porosity of single-layer LSM tapes sintered at 1320, 1350 and 1400°C for two hours was evaluated by mercury porosimetry (see Figure 52). For all of sintering temperatures, major pores in the sintered LSM tapes have a size of 1 µm. However, the total pore volume of LSM tape sintered at 1320°C is higher than tapes sintered at 1350 and 1400°C. There was a minor fraction (15-20 percent) of pores greater than 10 µm, which resulted from agglomeration of fine-scale carbon particles. SEM micrographs (Figure 53) of fracture cross sections confirmed that the tape sintered at 1320°C has significantly more fine-scale (1 µm) pores than tapes sintered at 1350 and 1400°C, as well as the presence of large pores inferred from porosimetry data. As shown by SEM data in Figure 54, sintered surfaces of these tapes show uniformly distributed pores of ~1 µm in size.
- **Density of sintered tapes.** It is difficult to measure densities of single layer tapes directly, (because they are only 40 µm thick). Densities calculated from porosimetry data were 55.7, 61.4 and 59 percent of theoretical for tapes sintered at 1320, 1350 and 1400°C, respectively (also consistent with SEM data).

Figure 52. The accumulation pore volume of LSM tapes with fine-scale carbon fugitive.

Figure 53. SEM micrographs of LSM tapes with fine-scale carbon fugitive (fractured surfaces).

Figure 54. SEM micrographs of LSM tapes with fine-scale carbon fugitive (sintered surfaces).

Bi-layer Cathode Substrates

In addition to providing mechanical support for the SOFC, the optimum cathode substrate also must provide additional functionalities: (1) high gas permeability to allow unimpeded air flow to the electrolyte; (2) maximum triple-phase boundary area at the cathode/electrolyte interface for enhanced electrochemical reactions; and (3) a sufficiently smooth surface for deposition of high quality interlayer and electrolyte films. A relatively large pore size is desired to maintain high gas permeability (to minimize Knudsen diffusion constraints), whereas fine-scale porosity is desired to increase triple-phase boundary volume and to provide a smooth surface for coating deposition. Thus, a multilayer cathode substrate strategy was adapted, by laminating a single LSM layer tape (with fine-scale carbon fugitive) with several LSM tape layers (with coarse carbon fugitives). Upon sintering at 1350°C, flat substrates were obtained with the cross-sectional microstructure shown in Figure 55. For this particular substrate, the layer with fine-scale porosity was about 40 microns thick. Several process refinement iterations were performed to improve quality of the bi-layer substrates – specifically to provide surfaces that are suited for subsequent deposition of dense electrolyte layers. One approach used for optimizing the fine-pore layer of bi-layer substrates was classification of carbon powder. This provided fine carbon particles of about one micron in size (see Figure 56). LSM tapes were produced by tape casting of slurries containing classified carbon powder, and laminated substrates were sintered at 1350°C for two hours. SEM micrographs (shown in Figure 57) confirmed a 2-micron pore size, both in cross section and on as-sintered surfaces.

Figure 55. The cross section of bi-layer LSM substrate with fine and coarse carbon fugitives, sintered at 1350°C.

Figure 56. SEM micrograph of classified carbon fugitive particles.

Figure 57. SEM micrograph of cross-section and surface of sintered LSM tape prepared with classified carbon fugitive.

In subsequent studies aimed at spin-coating deposition of interlayer and electrolyte films, it became apparent that the addition of pore formers in the top cathode layer was problematic with regard to achieve dense films. Thus, fabrication of the graded-pore substrate was modified with carbon fugitive particles omitted from the tape forming the top layer. By controlling particle size of the starting LSM powder, it was possible to achieve the desired pore size in the top layer. Resulting graded-pore substrates were flat and smooth, with the largest surface pores being in the order of 2 μm (see Figure 58).

Ceria Interlayer and YSZ Electrolyte Films

The use of ceria as an interlayer at the cathode/electrolyte interface is known to reduce interfacial resistance of cathode/electrolyte interfaces. For UMR's process, ceria interlayer was used for a secondary purpose – to achieve a smooth surface for subsequent YSZ electrolyte deposition. UMR's polymeric precursor process was modified to produce ceria interlayers. Nanocrystalline ceria powder was dispersed into a polymeric precursor solution, and ceria films were deposited by spin-coating of this suspension onto previously described graded-porosity cathode substrates. Details on the procedure are provided in Figure 59, and microstructures of ceria interlayer films are shown in Figures 60 and 61. As can be seen, this process yields essentially defect-free ceria films, which provided an extremely smooth surface. With these ceria interlayer films, UMR was able to demonstrate the deposition of high-density YSZ electrolyte films (see Figures 62 and 63).

Figure 58. SEM micrograph of double-layer cathode substrate made without carbon fugitive in the top layer (sintered at 1350°C).

Figure 59. Schematic of process used for depositing dense and nano-crystalline ceria interlayer films on LSM substrates, and SEM micrographs of ceria interlayer films.

Figure 60. Microstructure of ceria interlayer films deposited on porous LSM cathode substrates (films were annealed at 400°C, thickness of these interlayer films is ~0.5 microns).

Figure 61. Microstructure of ceria interlayer films deposited on porous LSM cathode substrates (films were annealed at 400°C, thickness of these interlayer films is ~0.5 microns).

Figure 62. Cross-sectional micrographs of an ultra-thin YSZ electrolyte film on LSM cathode substrates with a nano-porous ceria interlayer.

Figure 63. SEM micrographs of top surfaces of ceria interlayer film (upper left) and thin YSZ electrolyte film (lower right).

Phase II Conclusions

Development work in Phase II focused on three different fabrication routes for planar SOFC elements. NexTech developed tape-casting, colloidal-spray deposition, and co-sintering methods for cathode and anode supported elements. Ohio State University supported NexTech's process development work with novel characterization methods. ORNL established tape casting, screen-printing and co-sintering methods for anode-supported elements. UMR developed tape casting, colloidal processing, and spin-coating methods for cathode-supported elements having nano-crystalline YSZ electrolyte films. There was a high level of collaboration in Phase II, which contributed greatly to the successful outcome of the development efforts. The results of Phase II work at NexTech, Ohio State, ORNL and UMR are summarized below.

- Processes have been established at NexTech for the reproducible and reliable production of phase-pure perovskite lanthanum strontium manganite (LSM) cathode powder at a scale of up to 10 kilograms per week. Characteristics of this powder include a one-micron particle size and a surface area of 7-8 m²/gram. Electrical conductivity measured on dense LSM ceramic samples was similar to those obtained in the literature.
- Processes have been established at NexTech for the high yield and low cost production of dispersed suspensions of nanoscale yttrium-stabilized zirconia (YSZ) electrolyte material. These aqueous suspensions are critical components of NexTech's colloidal spray deposition process for YSZ electrolyte films.
- NexTech adapted a composite interlayer approach has been demonstrated for the fabrication of cathode-supported electrolyte films. The interlayer, a composite of praseodymium strontium manganese iron oxide (PSMF), was designed to prevent adverse reactions between the LSM cathode substrate and the YSZ electrolyte films and to improve low-temperature cathode performance.
- Tape casting and lamination processes were developed at NexTech and UMR for porous LSM cathode substrates, and at NexTech and ORNL for NiO/YSZ anode substrates. The key to achieving optimum porosity of sintered substrates is the incorporation of suitable pore-forming fugitive materials into the tape casting slurries. Keys to maintaining flatness of these substrates during sintering (or co-sintering) is optimization of the lamination conditions and binder burnout conditions, incorporation of an annealing step after lamination, and minimizing temperature gradients during binder burnout and sintering.
- A colloidal spray deposition process for YSZ electrolyte films was developed at NexTech, which utilizes an engineered YSZ suspension. The key to achieving high green densities and low sintering temperatures of these colloidally deposited films is tailoring the rheology and particle size distribution of the YSZ suspension. This process was scaled to large substrate areas using an automated ultrasonic spray deposition system that provides exceptional thickness uniformity of deposited films.
- ORNL developed a screen-printing process for depositing YSZ electrolyte films on green NiO/YSZ anode substrates. ORNL's screen-printing process allowed the thickness of the YSZ electrolyte films (after sintering) to be controlled within the range of 10 to 30 microns. The keys to ORNL's screen-printing process were the use of a proprietary ink formulation, the use of a three-roll mill for ink preparation, and selection of desired screen characteristics.

- Co-sintering processes for cathode-supported and anode-supported electrolyte elements were established at NexTech and ORNL. Co-sintered laminates had the desired morphology, with dense electrolyte films and porous electrode substrates. ORNL's process was scaled up to 100 cm² element areas and NexTech's process was scaled up to 50-cm² element areas. Both the NexTech and ORNL processes provide electrolyte elements with flatness required for the SOFC application.
- In collaboration with NexTech, Ohio State University established both laser dilatometry and optical profilometry as useful process development tools. Laser dilatometry is a non-contact method for evaluating shrinkage and curvature development during sintering, and optical profilometry provides quantitative measures of curvature and/or surface topography in sintered laminates.
- UMR established "graded-cathode" and "integrated interlayer/electrolyte" approaches for the fabrication of cathode-supported elements with nano-crystalline and ultra-high conductivity YSZ electrolyte films. With these approaches, UMR was able to demonstrate the fabrication of SOFC elements comprising ultra-thin, spin-coated electrolyte films on a porous cathode substrate.
- UMR established that nano-crystalline scandium-stabilized zirconia (ScSZ) films exhibit increased *electronic* conductivity at low oxygen partial pressures. This result contrasts to the increased *ionic* conductivity observed in nano-crystalline YSZ films. With high electronic (and ionic) conductivity, scandium-doped zirconia has potential to be used as an anode interlayer to improve performance.

PHASE III: SCALE-UP AND COMPREHENSIVE TESTING

Phase III Overview

The work in Phase III involved sample fabrication work at NexTech, ORNL, and UMR, with testing and characterization work at Northwestern, GTI, Ohio State and NexTech. The work in Phase III was conducted over a period of 2½ years, with several modifications in scope based on results obtained. The primary scope modification, early in Phase III, was to abandon cathode-supported cells that were being fabricated at NexTech in Track 1. This decision was based on difficulties in achieving technically viable power densities in button-cell tests. Thus, NexTech's effort was refocused toward development and scale-up fabrication processes for anode-supported cells. This development work was successfully completed and a multitude of samples were prepared for button-cell testing (at Northwestern University) and single-cell testing (conducted both at GTI and at NexTech). The primary challenge addressed by NexTech in Phase III was achieving required flatness levels in large-area anode-supported cells, while maintaining desired electrochemical performance. Another successful result of NexTech's effort in Phase III was the demonstration of highly active composite cathode materials, which allowed high SOFC performance levels to be achieved. ORNL continued development of fabrication processes for anode-supported cells, and provided samples to Northwestern for button-cell testing. UMR continued their process development work aimed at integration of cathode-supported cells with ultra-thin electrolytes. Ohio State University continued their work on development of laser dilatometry and optical profilometry as non-destructive evaluation methods for characterization of SOFC manufacturing process. NexTech fabricated a number of porous anode and cathode substrates for mechanical property testing at ORNL and Ohio State (in a non-DOE-funded collaboration).

Phase III Results and Discussion

Phase III results are described and discussed in the following sections.

Cathode Supported Cells

Early in Phase III, NexTech continued to develop cathode-supported cells and produced several samples of cathode-supported elements for button-cell testing at Northwestern. These elements comprised porous cathode (LSM) supports (~1mm thick), porous composite (PSM/GDC) interlayer films (5~10 microns thick), and dense electrolyte (YSZ) electrolyte films (~10 microns thick). A typical SEM microstructure is shown in Figure 62, which shows that targeted porous substrate and interlayer morphologies, along with high-density electrolyte films were achieved. NiO/GDC anodes were applied at Northwestern using existing screen-printing and annealing methods. In all cases, SOFC performance levels were well below expectations (open circuit voltages of less than 0.9 volts and maximum power densities below 100 mW/cm²). SEM microstructure analyses, in conjunction with energy dispersive spectroscopy (EDS) analyses were conducted to determine possible causes for the poor performance. Data is presented in Figure 64, which suggested that the cause for the low performance was lanthanum zirconate formation, presumably caused by diffusion of zirconium from the YSZ electrolyte through the PSM/GDC interlayer and reaction with lanthanum from the LSM cathode. After several trials with no significant performance improvements, a decision was made to abandon cathode-supported cells and re-focus NexTech's Phase III work on anode-supported cells.

Figure 64. Cathode-supported planar element with composite (PSM/GDC interlayer and YSZ electrolyte film): Cross-sectional SEM micrographs (a, b); and energy-dispersive spectrographic maps for zirconium (c), lanthanum (d), manganese (e) and praseodymium (f), corresponding to the SEM micrograph in (b).

Screen-Printed Cathode Coatings

With the decision to pursue anode-supported cells came the need to establish a screen-printing process for cathode coatings. A composite materials approach was pursued, whereby perovskite-structured electrode materials were mixed with gadolinium-doped ceria (GDC-10) electrolyte material. The process used to prepare composite cathode coatings is outlined in Figure 65; compositions of the component LSF and LSCF powders are provided below:

- LSF-20: $(\text{La}_{0.80}\text{Sr}_{0.20})\text{FeO}_3$
- LSF-40: $(\text{La}_{0.60}\text{Sr}_{0.40})\text{FeO}_3$
- LSCF: $(\text{La}_{0.80}\text{Sr}_{0.20})(\text{Co}_{0.20}\text{Fe}_{0.80})\text{O}_3$

The LSF and LSCF electrode powders with surface areas of 5-10 m²/gram were prepared using traditional milling and calcination methods. Electrical conductivity data obtained on dense ceramics of these compositions are presented in Figure 66. Nanoscale GDC-10 powder was prepared by NexTech's existing hydrothermal synthesis processes (and in some cases calcined to reduce surface area). Composite powder mixtures, with GDC contents ranging from 25 to 50 volume percent, were prepared by either ball milling or attrition milling. The mixed powders were then calcined at different temperatures (900 to 1050°C), sieved through a 200-mesh screen, and processed into inks using a three-roll mill. For each formulation, coatings were screen printed onto GDC electrolyte discs, and annealing studies were carried out to determine the minimum annealing temperature for obtaining adherent coatings (as characterized by the scotch-tape method). LSF-based coatings required annealing temperatures of 950 to 1000°C, and LSCF-based coatings typically required temperatures of 900 to 950°C. SEM micrographs of screen-printed composite cathode coatings are shown in Figure 67, which indicate a high degree of thickness and compositional uniformity.

Figure 65. Screen printing of composite cathodes.

Figure 66. Electrical conductivity of single-phase perovskite electrode materials.

Figure 67. SEM and BSE micrographs of screen-printed composite cathode coatings.

Electrode resistance measurements were made by a two-lead method. Samples were prepared by printing circular patterns (1.27 cm diameter) onto opposite faces of 300-micron GDC discs (which had been machined to precise dimensions). Silver paste was then applied to the electrode faces, and two silver lead wires (one for current and one for voltage) attached to each electrode. Electrical resistances measured on these symmetrically electroded GDC discs corresponded to the sum of the electrode resistance and the GDC electrolyte resistance (calculated from electrolyte resistivity and sample geometry). These modified two-point measurements were conducted over the temperature range of 400 to 800°C, using a digital voltmeter (with micro-amp current levels). At higher temperatures (above 700°C), were performed by applying a constant current (up to 1 amp/cm²) and measuring the resulting voltage. This I-V method only could be used at high temperatures (because of the potential for ohmic heating at lower temperatures), but it gives a more practical measure of cathode resistance (because SOFCs will operate at relatively high current levels). Although the subtractive method used for calculating electrode resistances has some inherent error, the method is straightforward and provides excellent comparative data. Results of the cathode formulation development studies are discussed below:

- Our work has confirmed the beneficial effect of adding GDC to LSF (and LSCF) cathodes, as is shown by data in Figures 68 and 69. Arrhenius plots of electrode resistance always showed the presence of two slopes, corresponding to a shift in activation energy. We attribute this to a regime of charge-transfer limited performance at lower temperatures and a regime of mass-transfer limited electrode performance at higher temperatures. However, this observation is in direct contrast to results in the literature, where linear Arrhenius behavior always is either observed or assumed. A comparison of results obtained for the two-lead and I-V methods is shown in Figure 70. The I-V method provides a significantly lower estimate of electrode resistance.
- There is a critical balance between maximizing surface area for electrochemical reactions (to reduce interfacial resistance) and maintaining intimate particle-to-particle contact within the highly conducting LSCF phase (to reduce sheet resistance). Thus, composite cathodes may best be utilized with bi-layer strategies – a composite cathode layer (e.g., LSF/GDC) applied at the electrolyte interface to facilitate electrochemical reactions, and a single-phase cathode layer LSCF layer then will be deposited to provide a current carrying function.
- The processing of the composite cathode material also was found to be critically important, both with respect to performance and to developing a practical screen printing process. For example, inks prepared from composite powders with surface areas of more than 10 m²/gram required multiple prints to build up a reasonable thickness (our target being 50 microns). Further, relatively poor performance was observed for cathodes prepared from high surface area composite powders. The best results were obtained when a pre-calcination step was added after attrition milling of coarse LSF (or LSCF) and nanoscale GDC powder.
- The optimum pre-calcination temperature (prior to ink preparation) for a composite cathode depended on composition – both the specific perovskite and the GDC content. This is shown in Figure 71, and summarized in Table 13. The ranking of performance levels follows the trend: LSCF/GDC > LSF-40/GDC > LSF-20/GDC, which is consistent with results from the literature. From the results, the optimum GDC content appears to be 40 volume percent.

Figure 68. Arrhenius plots of specific resistance for LSF-40 and LSF/GDC cathode coatings.

Figure 69. Arrhenius plots of specific resistance for LSCF and LSCF/GDC cathode coatings.

Figure 70. Comparison of specific resistance of LSCF/GDC electrodes, measured by the 2-lead and I-V methods

Figure 71. Effect of calcination temperature on interfacial resistance of composite cathodes of different formulations.

Table 13. Summary of Electrode Resistance Measurements			
Perovskite	GDC (volume%)	Pre-Calcination Temperature (°C)	Electrode Resistivity at 700°C ($\Omega\text{-cm}^2$)
LSF-40	30	1000	0.363
	40	950	0.273
	50	1000	0.475
LSF-20	30	1000	0.346
LSCF	30	900	0.184
	50	1000	0.615

Fabrication of Anode-Supported Cells

A considerable amount of work in Phase III was aimed at additional development and scale-up of fabrication processes for anode-supported cells. Initially, the focus was on demonstrating the performance in button-cell SOFC testing at Northwestern, and to evaluate relative performance of composite cathode formulations (as described above). Subsequent work on anode-supported cells focused on scale-up to large areas (7-cm by 10-cm) required for single-cell testing at GTI (and later at NexTech). Our general approaches to producing anode-supported cells, along with variables that were evaluated, are shown in Figure 72. A number of process modifications were evaluated and adopted throughout the course of NexTech's process development and scale-up work, as summarized in Table 14, and discussed below:

- The original anode substrate fabrication method, established in Phase II, involved lamination (via warm pressing) of individual green tape layers to form green substrate with targeted thickness (0.5 to 1.0 mm). The tapes were fairly thin (<100 microns), which required a relatively large number of tape layers for each substrate. Thus, the tape formulations and casting methods were modified to increase the thickness per tape, thus reducing the number of tape layers per laminate.
- A second process modification involved a switch from uniaxial to isostatic pressure for the lamination step, which improved bonding between individual tape layers (see Figure 73) and also led to a more uniform green density within green anode substrates (which reduced curvature evolution during subsequent binder removal, pre-calcination and sintering steps). Optimizing the isostatic lamination step involved changes to the plasticizer content in the tape formulation (see Figure 74) and the temperatures and pressures used during lamination (see Figure 75).
- Several approaches were evaluated for controlling anode microstructure, including different particle size distributions of NiO and YSZ powders, alternative pore forming materials (e.g., starches) and varying amounts of pore-formers. The effect of different pore formers on the microstructure of sintered anode substrates is shown in Figure 76. Microstructure of anode substrates fabricated without pore formers, by optimizing particle size distribution of the NiO and YSZ starting powders, is shown in Figure 77.

Figure 72: Fabrication methods used in the production of anode-supported cells.

- For most of the work in Phase III, NexTech's electrolyte deposition approach was based on a patent-pending ultrasonic spray deposition process. The core to the process is an aqueous coating suspension with a bi-modal particle size distribution. The coating suspensions were prepared by mixing a dispersed suspension of "nanoscale" YSZ particles (~50 nm size) with a dispersed suspension of "coarser" YSZ particles (~200 to 500 nm in size). The nanoscale YSZ fraction typically comprises ~20 percent of the YSZ content of the coating suspension. The coatings were sprayed onto pre-calcined anode substrates using the ultrasonic spray system (previously shown in Figure 26), and the YSZ-coated anodes then were sintered at temperatures of 1300 to 1400°C to densify the YSZ coatings and complete densification of the anode substrates.
- One of the challenges associated with the developed co-sintering process is that different anode formulations provide different sintering shrinkage behaviors (see Figure 78). Thus, a "calibrations" of pre-calcination and sintering shrinkages were required as new anode formulations were implemented (see Figure 79).

Table 14. Evolution of NexTech's process development efforts for anode-supported cells.			
Project Phase	Generation	Fabrication of Anode Substrates	Electrolyte Deposition and Co-Sintering
II	1	Tape casting of ball milled mixtures of NiO (GFS), YSZ (Tosoh), and 30 vol% pore former (rice starch). Lamination via warm uniaxial pressing. Binder burnout and anode pre-calcination. 1-mm thick anode substrates.	Coating suspension prepared from NexTech YSZ fines and Tosoh YSZ coarse particles. Ultrasonic spray deposition. Co-sintering at 1400°C.
II	2	Same as above, with alternative pore former (maltodextrin).	Same as above.
III	3	Same as above, with alternative NiO powder (Novamet) and lamination via warm isostatic pressing.	Same as above, with alternative YSZ powder (Viking) used for coarse fraction spray suspensions.
III	4	Same as above, with pore former comprising mixtures of rice starch and maltodextrin.	Same as above.
III	5	Same as above, with 30 vol% pore former (rice starch). Tape casting formulations modified to improve bonding during isostatic lamination.	Same as above.
III	6	Same as above, with increased pore former content (46 vol% rice starch). Lamination method modified to improve thickness uniformity. Evaluated thinner anode substrates (0.5 and 0.7 mm).	Same as above.
III	7	Same as above (0.7 mm thick anode substrates).	Same as above, with alternative YSZ powders (Unitec and Dai-Ichi) used as coarse fraction in spray suspensions. Sintering at 1300 to 1400°C.
III	8	Anode tapes produced from attrition milled mixtures of NiO and YSZ powders (0.7 mm thick anode substrates).	Screen printing of ScSZ electrolyte films on pre-calcined anode substrates. Sintering at 1300 to 1400°C.
III	9	Anode tapes produced from ball milled mixtures of NiO and YSZ powders with different particle sizes, without pore formers (0.7 mm thick anode substrates).	Screen printing of ScSZ electrolyte films on pre-calcined anode substrates. Sintering at 1300 to 1400°C.
III	10	Same as above.	Screen printing of anode interlayer and ScSZ electrolyte films on green anode substrates. Sintering at 1350 to 1400°C.

Figure 73. Effect of lamination method on morphology of sintered anode substrates fabricated by: (a) warm uniaxial pressing; and (b) warm isostatic pressing.

Figure 74. Effect of plasticizer content in tape casting formulation on the morphology of anode substrates fabricated via isostatic lamination and sintered at 1400°C.

Figure 75. Effect of isostatic lamination conditions on morphology of sintered anode substrates: 73°C/6.9MPa (a); 73°C/13.8MPa (b); 80°C/6.9MPa (c); and 80°C/13.8MPa.

Figure 76. Effect of different pore formers on microstructure of sintered anode substrates.

Figure 77. Microstructure of porous anode substrates produced without pore formers.

Figure 78. Shrinkage versus temperature for anode substrates: (a) ball milled NiO/YSZ powder mixture with pore former; (b) attrition milled NiO/YSZ powder mixture with pore former; and (c) ball milled mixture of coarse NiO/YSZ powder without pore former.

Figure 79. Lateral shrinkage of anode substrates during pre-calcination step, and total substrate shrinkage after sintering at 1400°C. Note that total shrinkage is independent of pre-calcination temperature.

- A second control parameter used for optimizing the co-sintering process was the relative particle sizes and amounts of the nanoscale and coarse YSZ fractions in the aqueous coating suspensions used for electrolyte deposition. In all cases, the nanoscale fraction was produced by NexTech's hydrothermal synthesis process (as was shown in Figure 25). As the relative amount of nanoscale YSZ fraction in the coating suspension was increased, the sintering temperature range shifted to lower temperatures and higher overall substrate shrinkage was required for full densification of the coating. Conversely, as the relative amount of coarse YSZ fraction was increased, the sintering range shifted to higher temperatures and less substrate shrinkage was required for full densification of the coating. A final control parameter was the specific YSZ material used as the coarse fraction. Several commercial YSZ materials (all with different particle sizes) were evaluated as the coarse fraction and successfully utilized in the process (see Figure 80).
- Alternative process modifications were implemented at NexTech during the later stages of Phase III, including the incorporation of interlayer films between the anode and electrolyte coatings and the replacement of YSZ with a scandium-stabilized zirconia (ScSZ) electrolyte composition. For this work, anode substrates were prepared with and without pore formers, and anode interlayer films and electrolyte films were applied by screen printing. When pore formers were not used, particle size distributions of the NiO/YSZ anode powders were controlled to provide targeted porosity levels after sintering. The anode interlayers were comprised of a fine-scale mixture of NiO and YSZ powders (without pore former). ScSZ electrolyte films were produced by screen printing from inks prepared using a commercially available powder. Example micrographs of anode-supported cells with screen-printed anode interlayer and ScSZ electrolyte films are shown in Figures 81 and 82.

Figure 80. Anode-supported YSZ electrolyte films, with different YSZ powders used as the coarse fraction of the coating suspensions: (a) Viking, sintered at 1400°C; (b) Viking, sintered at 1300°C; (c) Dai-ichi, sintered at 1350°C; and (d) Unitec, sintered at 1300°C.

- One of the key challenges addressed by NexTech's process development work in Phase III was eliminating curvature (camber) from co-sintered elements, especially as cell areas were increased. Several approaches were pursued, including optimization of processing methods to reduce sintering shrinkage mismatches between the anode substrate and electrolyte films (as discussed earlier), application of weights during sintering (constrained sintering), and/or post-sintering heat treatments with weights applied (creep flattening). Complete elimination of curvature was not achieved, although significant progress was achieved – at least to the extent that it was possible to perform single-cell testing of large-area planar cells.
- There is a trade-off between anode substrate thickness, stiffness of cells, and total curvature in these cells. It was found that with anode substrate thicknesses of 1000 microns, it was possible to achieve total curvature values of less than 100 microns. However, these thick cells were extremely stiff and fractured when loads were applied during cell testing. As anode substrate thicknesses were reduced to 500 microns, curvature increased to levels of 1000 microns and larger – however, these cells were fairly compliant. A good compromise was found to be at 700 microns anode thickness – reasonable flatness levels were achieved while cells are still compliant.

Figure 81. SEM and BSE micrographs of anode-supported, fabricated by screen printing of NiO/YSZ interlayer and ScSZ electrolyte films onto pre-calcined NiO/YSZ anode substrates (with pre formers), and sintering at 1350°C for two hours.

Figure 82. SEM and BSE micrographs of anode-supported, fabricated by screen printing of NiO/YSZ interlayer and ScSZ electrolyte films onto green NiO/YSZ anode substrates (without pore formers), followed by binder removal and sintering at 1400°C for two hours.

Button-Cell Testing

A number of anode-supported cells were fabricated at ORNL and at NexTech, and subjected to SOFC performance testing at Northwestern University. These cells, typically 1.5-cm diameter discs were tested using Northwestern's standard button-cell testing methods, with humidified hydrogen as fuel and air as oxidant. These data are presented in Table 15 and Figures 83-90, and summarized below:

- Anode-supported cells that were fabricated at ORNL, with LSCF-based cathodes deposited at Northwestern, demonstrated good performance levels (power densities up to 900 mW/cm² at 0.7 volts and 800°C), despite slightly low open circuit voltages (0.99 volts at 800°C). The improved performance levels were achieved by incorporating anode interlayers and increasing density of the electrolyte films (see Figure 83).
- Initial work at NexTech involved fabrication of anode-supported cells using anode substrates fabricated at ORNL. With LSCF/GDC cathodes applied, these cells also exhibited low OCV values (0.993 volts at 800°C) and lower performance (515 mW/cm² at 0.7 volts and 800°C) than those of previously described ORNL-fabricated cells (see Figure 84).
- As NexTech's cell development efforts evolved into Generations 4 and 5 (as previously described in Table 14), a number of cells were produced that provided expected OCV values (>1 volts) and good performance (500~1200 mW/cm² at 0.7 volts and 800°C). At this point, a number of identical cells (Generation 5) were fabricated and used as a platform for evaluating performance of screen-printed cathodes. Based on the results obtained, relative performances of composite cathode formulations are ranked in Table 16. Although the data do not provide absolute certainty, two conclusions can be drawn:
 - LSF/GDC cathodes outperformed LSCF/GDC and LSCF/PrDC cathodes at the extremes over the entire range of operating temperature.
 - GDC-10 provides better performance than GDC-20 when used as the electrolyte phase in composite cathodes.

Table 16. Ranking of cathode performance based on button-cell test results.			
Cathode Formulation	SOFC Performance (mW/cm² at 0.7 volts)		
	T = 600°C	T = 800°C	Figure
LSCF/PrDC-20	57	570	86
LSCF/GDC-20	20-56	267-515	87
LSCF-GDC-10	25	543-790	88
LSF-40/GDC-20	70-103	813-854	89
LSF-40/GDC-10	128-190	779-1170	90

Table 15. SOFC performance data obtained at Northwestern University using button-cell testing methods.							
Sample Number	Sample Description	Cathode Material	Supporting Figures	SOFC Performance Data			
				T (°C)	OCV (volts)	Power Density (W/cm ² at 0.7 V)	ASR (Ω-cm ²)
ORNL-1	Anode supported elements fabricated at Oak Ridge National Laboratory	LSCF/GDC (Northwestern)		600	0.93	4	29.0
				650	0.93	29	3.78
				700	0.97	95	1.65
				750	0.96	225	0.80
				800	0.94	372	0.46
ORNL-2	Anode supported elements fabricated at Oak Ridge National Laboratory	LSCF/GDC (Northwestern)	SOFC Data (Fig. 83)	600	1.04	187	1.22
				650	1.03	356	0.71
				750	1.01	730	0.31
				800	0.99	887	0.24
102-137C	Anode substrates fabricated at ORNL. YSZ films deposited at NexTech on pre-calcined substrates, cells were co-sintered at 1400°C	LSCF/GDC 30% GDC-20	SOFC Data (Fig. 84)	600	0.961	37	4.24
				650	1.004	105	2.15
				700	1.004	198	1.13
				750	1.006	340	0.65
				800	0.993	515	0.40

Table 15. SOFC performance data (continued).

Sample Number	Sample Description	Cathode Material	Supporting Figures	SOFC Performance Data			
				T (°C)	OCV (volts)	Power Density (W/cm ² at 0.7 V)	ASR (Ω-cm ²)
92-80G	Generation IV Cells (see Table 14)	LSF/GDC 30% GDC-10 calcined 950°C		600	1.052	20	10.9
				650	1.053	90	3.00
				700	1.045	205	1.16
				750	1.027	388	0.44
				800	1.009	684	0.28
92-80W	Same as above	Same as above (duplicate)	SOFC Data (Fig. 85)	600	1.084	44	6.82
				650	1.081	140	2.18
				700	1.068	385	0.65
				750	1.054	685	0.32
				800	1.038	911	0.24
102-100B	Generation V Cells (see Table 14)	LSCF/PrDC 30% PrDC-20 calcined 950°C	OFC Data (Fig. 86)	600	1.106	57	4.02
				650	1.095	129	1.87
				700	1.084	238	1.03
				750	1.066	388	0.58
				800	1.053	570	0.41

Table 15. SOFC performance data (continued).

Sample Number	Sample Description	Cathode Material	Supporting Figures	SOFC Performance Data			
				T (°C)	OCV (volts)	Power Density (W/cm ² at 0.7 V)	ASR (Ω-cm ²)
102-100C	Generation V Cells (see Table 14)	LSCF/GDC 30% GDC-20 calcined 950°C	SOFC Data (Fig. 87)	600	1.086	56	4.19
				650	1.077	130	1.90
				700	1.074	160	1.46
				750	1.065	298	0.73
				800	1.044	515	0.43
102-100D	Generation V Cells (see Table 14)	Same as above (duplicate)		600	1.090	20	9.76
				650	1.089	54	4.19
				700	1.074	104	2.15
				750	1.057	184	1.25
				800	1.046	267	0.74
102-100E	Generation V Cells (see Table 14)	LSCF/GDC 30% GDC-10		700	1.092	179	1.44
				750	1.080	369	0.62
				800	1.025	543	0.38
102-100F	Generation V Cells (see Table 14)	Same as above (duplicate)	SOFC Data (Fig. 88)	600	1.063	25	8.41
				650	1.079	89	2.74
				700	1.071	225	1.08
				750	1.058	472	0.50
				800	1.043	790	0.28

Table 15. SOFC performance data (continued).

Sample Number	Sample Description	Cathode Material	Supporting Figures	SOFC Performance Data			
				T (°C)	OCV (volts)	Power Density (W/cm ² at 0.7 V)	ASR (Ω-cm ²)
102-100G	Generation V Cells (see Table 14)	LSF/GDC 40% GDC-20 Calcined 1000°C		600	1.086	103	2.47
				650	1.081	196	1.31
				700	1.069	368	0.67
				750	1.056	578	0.41
				800	1.037	813	0.28
102-100H	Generation V Cells (see Table 14)	Same as above (duplicate)	SOFC Data (Fig. 89)	600	1.080	70	3.29
				650	1.091	155	1.62
				700	1.080	314	0.78
				750	1.065	646	0.38
				800	1.050	854	0.26
102-100I	Generation V Cells (see Table 14)	LSF/GDC 40% GDC-10 calcined 1000°C	SOFC Data (Fig. 90)	600	1.091	190	1.58
				650	1.090	315	0.89
				700	1.078	560	0.46
				750	1.063	873	0.27
				800	1.049	1172	0.20
102-100J	Generation V Cells (see Table 14)	Same as above (duplicate)		600	1.106	128	2.34
				650	1.095	259	1.08
				700	1.082	448	0.58
				750	1.067	675	0.36
				800	1.052	779	0.29

Figure 83. SOFC performance data (Sample No. ORNL-2).

Figure 84. SOFC performance data (Sample No. 102-137C).

Figure 85. SOFC performance data (Sample No. 92-80W).

Figure 86. SOFC performance data (Sample No. 102-100B).

Figure 87. SOFC performance data (Sample No. 102-100C).

Figure 88. SOFC performance data (Sample No. 102-100F).

Figure 89. SOFC performance data (Sample No. 102-100H).

Figure 90. SOFC performance data (Sample No. 102-100I).

Testing of Large-Area Cells

Single-cell testing of large-area, anode-supported cells was conducted at the Gas Technology Institute (GTI) and at NexTech. GTI's testing approach involved the use of specially designed and machined Inconel-600 fixtures, which provide both gas manifolding and current collection functions. These fixtures accommodated planar cells (1-mm thickness) with 70-cm² total area (7-cm by 10-cm) and 35-cm² active cathode area (5-cm by 7-cm). The apparatus included block heaters, so that heat could be applied directly to the cell from both sides of the gas manifolds. A number of testing trials were attempted, with the cell test assembly, shown in Figure 91. GTI's general approach to testing involved the following:

- Cathode and anode current collection was facilitated by using silver and platinum mesh screens in contact with the cathode and anode faces, respectively (not shown in Figure 91).
- Several different gasket materials were fabricated at NexTech via tape casting and supplied to GTI. A number of different seal materials were evaluated, including talc, mica, and experimental seal materials under development at NexTech in a separately funded project.
- A clamping force (5-20 psi) was used to achieve seals, and in most cases, excellent seals were achieved at room temperature (as determined by measured gas compositions of the cathode and anode exhausts).
- Cells were heated up over under slow controlled cycles from room temperature to the cell operating temperature (800°C). During heat-up, air flowed through the cathode chamber at a rate of 800 cc/min, and a gas mixture of 90% N₂ and 10% H₂ flowed through the anode chamber at a rate of 400 cc/min. After the cell reached 800°C, the anode gas was switched to pure hydrogen (285 cc/min) to complete anode reduction and begin testing.
- In most cases, seals were lost by the time the cells reached the operating temperature, which led to very low open circuit voltages and poor performance, and shut-down of the test. Post mortem evaluations (see Figure 92) were performed for each of the tests. In most cases, the leaks were caused by cell cracking and/or seal failures, and were attributed to excessive cell curvature, thickness non-uniformities of cells, and excessively high clamping forces.
- In one case, reasonable data were obtained (see Figure 93), although OCV was low (965 mV) due to poor seal quality, and power density was correspondingly low (~200 mW/cm²). The data also suggest gas diffusion limitation (probably anode related) at higher current densities (>400 mA/cm²).

Throughout the course of this collaborative testing work with GTI, NexTech made significant improvements in cell quality (i.e., curvature was reduced from 500 microns to less than 100 microns, and cell thickness variations were reduced from 75 microns to less than 25 microns). However, it proved to be difficult to achieve cell flatness levels of less than 50 microns, which would have allowed successful testing of 1-mm thick anode supported cells using GTI's testing method. At this point, NexTech re-focused its cell fabrication work on reducing anode substrate thickness (500 to 700 microns), and established capability at NexTech to complete cell testing work on the project.

Figure 91. Testing methodology used at Gas Technology Institute for single-cell testing of large-area anode-supported cells.

Figure 92. Post-mortem evaluations: photograph of anode-side test fixture and anode face of cell (top); and photographs of cathode-side test fixture and cathode face of cell (bottom).

Figure 93. Cell performance data obtained at GTI on large-area anode supported cells.

Based on experience gained with GTI's cell testing work, NexTech successfully established a methodology for large-area cell tests (see Figure 94). The testing methodology is described as follows:

- Inconel-600 test fixtures were similar to those used at GTI, although these fixtures provided a slightly smaller active area of 28 cm² (4-cm by 7-cm). Steel tubes were welded into fixture to provide gas inlets and outlets, so that the cell test fixture could be placed in a tube furnace.
- The assembly was similar to that used by GTI, with silver-mesh cathode current collectors and platinum-mesh anode current collectors. A slight difference was the use of conductive inks to facilitate current collection from the active electrodes (nickel oxide ink at the anode and lanthanum manganite or cobaltite at the cathode).
- A different sealing strategy was adapted to prevent cracking of the cells during testing. Seal gaskets were cut from commercially available porous alumina "paper". No clamping force was applied – the only pressure applied to the cells and seals came from the weight of the top inconel fixture. This sealing method did not provide a perfect seal, but it did provide a means for testing under conditions of relatively high fuel and air utilizations (~25 percent).
- A final difference in the testing methodology was a change in the cell heat-up protocol. The cells were heated to the initial operating temperature (850°C), with air following through both the cathode and anode channels. Once the cell was at temperature, the anode gas was switched to nitrogen (to purge air from the line) and then to a mixture of N₂ and H₂ to initiate anode reduction.

Figure 94. Testing methodology used at NexTech Materials for single-cell testing of large-area planar SOFCs (shown for electrolyte-supported cell).

NexTech was able to successfully test two large-area cells with the modified method. The first cell test was performed with a Generation-9 cell with a screen-printed ScSZ electrolyte. The microstructure of this particular cell was presented earlier in Figure 81. Current-voltage curves were obtained over a temperature range of 650 to 850°C, with a hydrogen flow of 350 cc/min, which was humidified at about the three percent level (corresponding to a fuel utilization rate of 40 percent for a current density of 0.7 A/cm²). For this and subsequent tests, the air flow rate was held constant at 1,500 cc/min (corresponding to a fuel utilization rate of 20 percent for a current density of 0.7 A/cm²). As shown in Figure 95, under these conditions, the cell performed well with near-theoretical open circuit voltages and a power density of approximately 0.4 W/cm² at 0.7 volts at 800°C. After these data were obtained, the fuel was reduced and diluted with nitrogen (150 cc/min H₂ and 150 cc/min N₂), and data current-voltage curves were re-taken. As shown in Figure 96, under these diluted fuel conditions, the performance of this cell was reduced (with a power density of approximately 0.27 W/cm² at 0.7 volts at 800°C). Further, there was evidence of significant gas diffusion limitation at higher current densities (>400 mA/cm²).

The second cell test was performed with a Generation-10 cell with a screen-printed ScSZ electrolyte. The microstructure of this particular cell was presented earlier in Figure 82. For this test, problems were encountered with the seal, so the test could only be performed with relatively high fuel flow rate (300 cc/min of hydrogen, diluted with 200 cc/min of nitrogen). As shown in Figure 97, the cell exhibited a near theoretical open circuit voltage and a power density similar to that of the previous cell (~0.4 W/cm² at 0.7 volts at 800°C).

Figure 95. SOFC performance measured at NexTech for large-area cell (Generation-9) with hydrogen flow rate of 350 cc/min.

Figure 96. SOFC performance measured at NexTech for large-area cell (Generation-9) with diluted hydrogen as fuel.

Figure 97. SOFC performance measured at NexTech for large-area cell (Generation-10).

Non-Destructive Testing

Throughout this project, NexTech's fabrication process development work was augmented by laser dilatometry and optical profilometry studies at Ohio State. These tools provided new means of characterizing individual tapes, laminates, and sintered bi-layer elements. In addition to supporting NexTech's work, Ohio State focused much of its effort in Phase III to demonstrate unique attributes of their non-destructive evaluation tools. Some of this work was summarized in a manuscript that has been submitted for publication, which is attached as Appendix A. A few of the salient features of Ohio State's work in Phase III are summarized below.

Optical Profilometry, a tool adapted from use by the semiconductor industry, uses interference of filtered white light reflected from a surface as imaged by a CCD array to 'map' surface height versus horizontal distance. It is not contact-based (unlike existing stylus-based methods) and thus well-suited to examination of these relatively delicate fuel cell materials. Profilometry provides information *not* visible to the naked eye; if distributed across several square centimeters of area, curvatures of hundreds of microns cannot be seen, and certainly not quantified. While the technique has lower spatial resolution than SEM, it can provide both microstructural and macrostructural (curvature) data in a non-destructive manner within a dimensional regime that is of considerable importance to planar SOFC elements.

Figure 98 provides an example of the kind of information available from optical profilometry. This image represents a 1.5 x 2-inch corner of an node-supported cell fabricated at NexTech; the area analyzed compromises approximately 25% of the entire electrolyte-coated surface of the cell. With easily interpreted color coding, it is clear that the edge of the cell is non-uniform with regards to height. This is a critical issue as this edge eventually must be sealed within a stack to provide for gas tightness during operation. Obviously, any sealing stresses will be unevenly applied; interconnect integration to the surface also will be affected. Four other cells were analyzed in an identical manner – and each of the areas addressed by the scans exhibit unique curvature profiles.

Figure 98. Optical profilometry image showing curvature across the surface of a 3.5-cm by 5-cm corner of a 7-cm by 10-cm anode-supported cell. Blue represents the 'low' spots on the surface; red represents the 'high' spots.

Figure 99 is a higher resolution optical profilometry image of a densified electrolyte layer on an anode-supported cell. This image demonstrates that cracking due to compressive failure of the electrolyte layer can successfully be imaged non-destructively by the profilometer (this particular cell was fabricated with an electrolyte coating with less shrinkage than the anode substrate). In addition, other areas of the same cell demonstrate no cracking, suggesting that these stresses evolve locally as cells cool. In this case, sintering cracks have been observed as well as cracking due to mechanical failure of the electrolyte layer at much lower temperatures. Cracking of these electrolyte layers may be controlled by localized high spots and low spots that deviate from perfectly flat geometries. Out-of-plane stresses can develop in these real, as-fabricated cells and our expectation is that sealing/operating stresses will exacerbate these pre-existing cracks. The ability to detect such flaws is important with respect to quality control, and also will allow studies of electrolyte film damage under conditions of thermal cycling and/or anode reduction.

Figure 99. Crack pattern in an electrolyte layer as analyzed using optical profilometry.

One of the key attributes of optical microscopy is the potential process development and quality control tool for the manufacture of anode-supported SOFCs. The effects of specific processing steps (e.g., binder removal, sintering, sinter-forging, and cathode deposition) on curvature evolution are readily discernable. Another important demonstration in the project was the effect of anode on curvature evolution, as shown in Figure 100. These data show that the reduction of nickel oxide to nickel metal in the anode leads to a significant increase in curvature of anode-supported elements.

Surface Statistics:

R_A : 32.58 μm
 R_Q : 40.30 μm
 R_Z : 292.0 μm
 R_T : 316.7 μm

Surface Statistics:

R_A : 50.54 μm
 R_Q : 63.44 μm
 R_Z : 374.58 μm
 R_T : 389.8 μm

Figure 100. Optical profilometry scans of anode-supported planar elements before (top) and after (bottom) reduction of anode-supported cells.

Laser Dilatometry. One of the key historical limitations to the field of ceramics, and to solid oxide fuel cells in particular, derives from the fact that once the furnace door is closed all dimensional information about the sample ceases. After a variety of thermal dwells, different heating rates and thermal excursions the sample again becomes visible. This arrangement can make problem-solving quite difficult as it is impossible to know precisely at what specific temperature curvature developed, cracking took place, or when delamination occurred. This element of mystery is inappropriate for any ‘mature’ manufacturing process. It can best be described by characterizing the furnace as a “black box” that hides the processes occurring within.

OSU researchers use a laser micrometer having a repeatability of within 0.5 microns, integrated with a furnace (see Figure 101). The laser beam is scanned through a collimator lens in a parallel path across the sample toward a receiving lens. The receiving lens focuses the radiation into a photo detector. When the beam encounters the sample, it disrupts that part of the beam curtain path, creating a space devoid of light. This space creates a time signal that is processed and converted to a length measurement. A positioning motor controls the sample’s vertical position within the horizontal beam and is connected to the dilatometer output. As discussed earlier, laser dilatometry was found too be useful as a process development tool for evaluating sintering shrinkages during NexTech’s process development work in Phase II (see Figures 28-30).

Figure 101. Schematic diagram of the laser dilatometer used at Ohio State University.

A focus of Ohio State's work in Phase III was to expand the scope of useful information that can be obtained using laser dilatometry (outside the scope of sintering process characterization). For example, by collecting data using a rotational stage these segments can be connected to form a true three-dimensional view of a surface at any temperature of interest. Figure 102 provides an example of a three-dimensional reconstruction of a SOFC laminate at 1304°C. In this image, the curvature of the cell was reconstructed using the same color scheme as used for optical profilometry. This result illustrates that laser dilatometry can be used to follow the dimensional behavior of both single tapes and laminates/cells throughout any temperature excursion.

In addition to monitoring single tapes and laminates, the technique also was applied to examine the behavior of simple stacks as a function of heating. An experiment was designed whereby laser dilatometry was used to explore the behavior of seals within a simple stack comprised of alternating dense (YSZ) electrolyte plates interleaved with glass/ceramic composite seals (see Figure 103). The laser dilatometer was able to discern what individual components of the stack were doing during heating under load. For example, lateral displacements of up to 100 microns were observed upon melting of the glass phase in the seals. As shown in Figure 104, it also was possible to discern the expansion and shrinkage behavior of individual seal layer and to show that this shrinkage behavior was not repeated during thermal cycling.

Figure 102. Three-dimensional reconstruction of a SOFC laminate at 1304°C.

Figure 103. Laser dilatometry analysis of a model 'stack' during heating to 900°C. The laser beam provides dimensional and positional information about all components of the stack during the heating process.

Figure 104. Dimensional change of an individual seal (see Figure 103), which shows shrinkage during initial heating (pink line) and a different shrinkage profile during a subsequent thermal cycle (blue line).

Mechanical Property Testing

Throughout Phase III of this project, NexTech collaborated with other organizations to provide samples for mechanical property testing and other types of characterizations. A number of LSM cathode substrates and NiO/YSZ anode substrates (both reduced and un-reduced) were provided to ORNL for flexural strength tests, and results obtained at ORNL were presented at several SECA Core Technology Workshops. NexTech also provided anode and cathode substrates to Ohio State (Dr. Mark Walter of Ohio State's Mechanical Engineering Department), under an informal collaboration. Dr. Walter studied the effect of various anode reduction cycles on mechanical strength of the reduced substrates. The results of this work suggested that the anode reduction scheme has significant impact on microstructure and mechanical strength of anodes. A manuscript describing these results is presented as Appendix B.

Phase III Conclusions

- ❑ NexTech fabricated a number of cathode-supported electrolyte elements with targeted morphologies (i.e. porous LSM substrates, micro-porous ceria-based interlayers, and dense YSZ electrolyte films). A number of these cells (with anodes applied) were subjected to SOFC testing both at NexTech and Northwestern. *Power densities obtained on these cells were very low ($<100 \text{ mW/cm}^2$). For this reason, work on cathode-supported cells was abandoned and subsequent work focused on anode-supported cells.*
- ❑ SOFC testing has been conducted both at NexTech and at Northwestern University to establish baseline performance characteristics of anode-supported cells with LSF and LSCF based cathodes. *Maximum power densities in excess of 1 W/cm^2 at 800°C were achieved for anode-supported cells produced at NexTech and at ORNL.*
- ❑ Screen printing methods have been established at NexTech for high-performance composite cathode formulations in the LSF/GDC and LSCF/GDC systems. *Screen-printed composite cathodes were used in the NexTech cell that demonstrated high performance.*
- ❑ Laser dilatometry and optical profilometry have been established at Ohio State University as non-destructive techniques for process development and quality control. *NexTech used information obtained using these methods to design co-sintering cycles to improve flatness and quality of anode-supported and cathode-supported elements.*
- ❑ A number of porous anode and cathode substrates were prepared and subjected to mechanical property testing at ORNL and Ohio State (in a non-DOE-funded collaborative arrangement). *We have found that proper reduction conditions for anode substrates are important to maintaining strength.*
- ❑ NexTech scaled up their fabrication processes to make anode-supported cells with 7-cm by 10-cm areas that were required for single-cell tests at GTI and NexTech. *Achieving suitable flatness in large-area cells was found to be a significant challenge, which was addressed through several process modifications.*
- ❑ A single-cell testing methodology was established for large-area, anode-supported cells. *Performance levels of 400 mW/cm^2 (at 0.7 volts and 800°C) were achieved with relatively high fuel utilization rates.*

LIST OF ACRONYMS AND ABBREVIATIONS

UMR:	University of Missouri-Rolla
ORNL:	Oak Ridge National Laboratory
GTI:	Gas Technology Institute
MAC:	Michael A. Cobb & Company
AMT:	Advanced Materials Technologies (AMT)
EMTEC:	Edison Materials Technology Center
AMI:	Adaptive Materials, Inc.
SOFC:	Solid oxide fuel cell
SECA:	Solid State Energy Conversion Alliance
DOE:	U.S. Department of Energy
YSZ:	Yttrium stabilized zirconia
ScSZ:	Scandium stabilized zirconia
GDC:	Gadolinium doped ceria
SDC:	Samarium doped ceria
LSM:	Lanthanum strontium manganite
LSF:	Lanthanum strontium ferrite
LSCF:	Lanthanum strontium cobalt ferrite
PSM:	Praseodymium strontium manganite
PSMF:	Praseodymium strontium manganese ferrite
OCV:	Open circuit voltage
ASR:	Area-specific resistance
SEM:	Scanning electron microscopy
BSE:	Back-scatter electron mode
EDS:	Energy dispersive spectroscopy

Appendix A

Wenxia Li, Kathy Hasinska, Matt Seabaugh, Scott Swartz, and John Lannutti, *Curvature in Solid Oxide Fuel Cells*, submitted to Journal of Power Sources (accepted).

Appendix B

Yaou Wang, Mark E. Walter, Katarzyna Sabolsky, and Matthew Seabaugh, *Effects of Reduction Process Parameters on the Microstructure and Mechanical Properties of NiO/YSZ Anodes* (draft), to be submitted to Journal of Materials Science.

Curvature in solid oxide fuel cells

Wenxia Li^a, Kathy Hasinska^b, Matt Seabaugh^b, Scott Swartz^b, John Lannutti^{a*}

a. Department of Materials Science and Engineering, The Ohio State University,

2041 College Rd., Columbus, OH 43210

b. NexTech Materials Ltd, 404 Enterprise Dr., Lewis Center, OH 43035

*Corresponding author. Tel: 614-292-3926, Fax: 614-292-1537, E-mail:

lannutti.1@osu.edu

Abstract

At this point in history, curvature is inherent to the laminated components that comprise solid oxide fuel cells (SOFCs). Surprisingly, however, this fact has never been previously quantified in the literature. In addition, potential curvature changes associated with NiO reduction and re-oxidation during operation have not been investigated. In this report, an optical profilometer was employed to nondestructively quantify the surface curvature or cracking behavior observed on a large scale in industrially manufactured cells. This provides insights into the challenges that the component materials face as well as additional appreciation for why, in spite of a concerted effort to commercialize SOFC power generation, all currently manufactured SOFC stacks fail. Our results demonstrate that cracked electrolyte areas are flatter than uncracked regions. The height of the electrolyte surface ranged from 86 to 289 μm above the baseline following sintering. Reduction typically results in increases in curvature of up to 214 μm . Initial crack density appears to affect curvature evolution during reduction; the higher the crack density, the smaller the curvature increase following reduction at 600°C. Following oxidation at 750°C, large

changes in curvature (up to 280 μm) are noted that appear to be related to the strength of the bond between the electrolyte and the underlying anode.

Key words: warpage, glassy seals, leakage, electrochemical, hydrogen.

1. Introduction

A variety of stresses exist in solid oxide fuel cell stacks [1-4] . Stresses inherent to each cell may be caused by (1) differential sintering [4-6] ; (2) mismatches in thermal expansion between the electrolyte, anode and cathode layers [7] during operation; (3) applied assembly stresses exacerbated by curvature originating during tape casting and lamination and (4) stresses resulting from electrochemical operation, such as those due to thermal cycling or NiO reduction/redoxiation.

These stresses can lead to substantial differences in dimensional change either between or in each individual cell within a stack. Any mismatched dimensional response to heating during stack manufacturing or operation could lead to loss of stack integrity. For a given individual cell, such stresses could result in cracking of the electrolyte and subsequent failure of the cell and other cells around it.

Historically, those cracks typically observed in these multilayered composites are (1) channel cracking caused by tensile stresses that develop during sintering [8, 9] ; (2) so-called ‘mud’ cracks originating from differential drying or sintering [8] ; (3) layer delamination [2, 9] and (4) edge-effect cracking and delamination caused by compressive stresses [8, 9] . Cracks originating from differential drying and sintering processes appear to result in larger crack displacements than those originating from simple thermal mismatch [8, 9] . Either SEM or optical microscopy [8-10] is usually used to detect and observe the

behavior of these cracks. However, these two methods usually require destructive sample preparation. In addition, observing crack distributions across the entire surface of a single cell via SEM can be very time consuming as this technique only examines a relatively small area (around $2.5 \times 3 \text{ mm}^2$) even at its lowest magnifications.

The availability of nondestructive methods to characterize curvature or cracking behavior on a larger scale have thus become important in addressing long-standing “show stoppers” in the push to commercialize SOFC power generation. In this paper, an optical surface profilometer was employed to detect crack density distributions in the electrolyte layer of individual, industrially manufactured SOFCs. In addition, since the profilometer measures specimen surface height, scanning the surface of a cracked specimen before and after relevant heat treatments was used to examine the possible linkage between either curvature change or cracking and the corresponding chemical stresses anticipated during long term operation.

2. Experimental Procedure

Gadolinia stabilized ceria containing 10 mol% of gadolinia (GDC) and nickel oxide (NiO) were co-mixed at the 50 vol% Ni (m) level, tape cast and laser cut into circles 1 inch (25.4 mm) in diameter (NexTech Materials Ltd, Lewis Center, OH). These circles were laminated at 80°C and 2000 psi (14 MPa) to form anode substrates. By heating at 1°C/min to 600°C, these substrates were burned out at 600°C and then heated to 1250°C for one hour (at 5°C/min) to provide sufficient strength for handling. The lightly sintered substrates were then spray coated with a GDC electrolyte layer using an aerosol spray deposition process. The resulting samples were air dried and then sintered at either 1350 or 1400°C for

1 hour, respectively, utilizing a heating rate of 2°C/minute. The samples were sintered in groups of five, sandwiched between two 10 cm × 10 cm × 500 μm thick porous ceria-coated YSZ plates. The GDC electrolytes of one 1400°C-(labeled as 'A') and two 1350°C-sintered specimens ('B' and 'C') were examined using a non-contact surface profilometer (Wyko NT 3300, Veeco Metrology Group, Tucson, Arizona) following these sintering steps. R_z , the distance between the average of the top ten peaks and the average of the bottom ten valleys, was calculated to provide a quantitative estimate of the overall surface variation. For a more microstructural comparison, the specimens were carbon-coated and specific areas of the electrolyte surface were observed under SEM (XL-30 ESEM-FEG, Philips). In all cases we carefully monitored exactly the same area of the specimen following each thermal treatment.

To evaluate the effect of NiO reduction during operation of the fuel cell on curvature and cracking, these same specimens were reduced at 400°C for 2 hrs and at 600°C for 24 hrs, respectively, using a 5% H₂-N₂ atmosphere. To observe the effects of oxidation on curvature, these specimens were then oxidized in air at 750°C for 24 hrs. To confirm that reduction and oxidation were completed, the weight loss of three similar anode discs (25.4 mm in diameter) were measured following identical reduction and oxidation steps, respectively.

3. Results

3.1 Crack density versus sintering temperature

Fig. 1 shows electrolyte surface images obtained from the optical profilometer. The overall surface variation ($R_z = 289$) of specimen A sintered at 1400°C is much larger than that of

the specimens sintered at 1350°C ($R_z = 102$ and $86\text{ }\mu\text{m}$ for B and C, respectively). A key observation relevant to all cells examined to date is that even though specimens B and C are produced using exactly the same process, the curvature of each specimen is unique.

To better reveal smaller-scale surface features, the images shown in Fig. 2 are processed to remove the spherical surface curvature. Once this is done, a variety of cracks and crack sizes become clearly visible. Specimen A exhibits the highest crack density, specimen C the lowest. Images taken at higher magnifications on certain areas of the specimens (Fig. 3) indicate that the specimen sintered at higher temperature generates a complete network of cracks, while the specimens sintered at the lower temperature tend to display a more scattered array. In addition, the profilometry consistently shows that the crack edges are raised up relative to the surrounding surface. As observed during measurement of curvature, B and C display clear differences in both the pattern and density of cracking.

3.2 Crack density distribution versus position

To better understand the relationship of curvature behavior or residual stress and crack distribution, the crack density in the coating surface was estimated by magnifying the profilometry surface data. The results are schematically shown in Fig. 4. Twelve-color maps were employed to better illustrate the surface curvature of each specimen.

Paradoxically, this showed that wherever the surface appears to be the flattest corresponds to the location of the highest crack densities.

3.3 Comparison of profilometry and SEM

SEM was performed to provide higher resolution observations of crack morphology in comparison to the results of profilometry. Fig. 5 (a) and (b) shows a direct comparison of cracked and uncracked areas of the electrolyte. Consistency is apparent between the two

techniques. While the profilometer cannot detect or distinguish very small, micron-level cracks (see Fig. 5 (c)) it does clearly image the surrounding raised up areas and relate them to localized changes in curvature.

3.4 Surface curvature post reduction and oxidation

The weight loss behavior (Fig. 6) of the three specimens shows that reduction is nearly complete at 600°C. Following reduction, the surface morphology was examined using both profilometry and SEM (Figs. 5 (a) and 7 (a), (b)). Even using the higher resolutions inherent to SEM, no obvious microstructural changes are observed (compare Figs. 5(c) and 7 (c)) except that the surface in the upper right hand of Fig. 7(c) appears to be higher. However, profilometry shows that reduction increases the overall surface variation by approximately 30 to 40 μm for A and B and 200 μm for C (Fig. 8). The plots generated following reduction at 400 and 600°C also indicate that the overall curvature increases are initiated at the edge of these specimens.

Following the rapid oxidation of these reduced specimens, the overall curvature of samples A and B increased by approximately 280 and 200 μm , respectively, while that of specimen C remained almost unchanged. Again, Fig. 6 shows that the three anode specimens were fully oxidized following exposure to 750°C. Profilometry shows that the localized curvature near the edge of the specimen increases (Fig. 9). Delamination of the anode layers was observed in those edges close to the electrolyte layers showing the greatest damage (Fig. 2). In some cases, SEM shows that this abrupt curvature change resulted in a greater density of new cracks in the electrolyte layer (Fig. 10).

4. Discussion

4.1 Overall surface curvature, crack density and residual stress

During densification, these specimens curved toward the anode substrate even while under constraint. The overall surface variation increased as the sintering temperature increased (Fig. 1 color bar). Mismatched sintering shrinkage of the different layers provides a potential explanation. The electrolyte layer reaches full density while the anode layers are still quite porous. The higher the sintering temperature, the greater the shrinkage experienced by the anode layers and, therefore, the greater shrinkage differences generated between the anode and the already dense electrolyte. Compressive stresses generated in the electrolyte can then lead to cracking. Lower sintering temperatures apparently resulted in smaller shrinkage differences and lower crack densities. Once the overall curvature is subtracted from the profilometry images, the crack densities in the electrolyte layers can be clearly resolved. The higher the sintering temperature, the greater the shrinkage differences between the two components and, therefore, a greater incidence of network cracks were observed in the electrolyte coating (Figs. 2 and 3).

In general, the curvature of a dense electrolyte of a multilayer composite specimen should be a combination of prior manufacturing and current residual stresses. Larger curvatures likely reflect a larger residual stress. Once the residual stress in the electrolyte layer goes above a critical level, cracks occur and stress is released [10]. In Fig. 4, the areas in which the surface height changes rapidly appear to have either a low crack density or no cracks at all. This suggests that high residual mismatch stresses are concentrated around those areas. In the cracked areas, this same mismatch stress is released by cracking and the residual stress (if any) is small and this produces the relatively flat areas shown in the color maps of Fig. 4. In addition, the constraint on top of the specimen during sintering likely contributes both to the flatness (via gravimetric constraint) and to cracking (via frictional constraint).

These areas are those in which manufacturing stresses leading to curvature were concentrated and contacted the constraining surface with the greatest force.

The overall surface curvature increased during reduction as shown in Fig. 8. All specimens curved even more toward the anode layer (see Fig. 8) probably due to the additional shrinkage generated by the reduction of the NiO to Ni [11]. This indicates that reduction must produce at least some stresses within the specimen. Because little or no constraint exists at the edges of the specimen, these free edges tend to deform preferentially to release the shrinkage stresses caused by reduction. Surprisingly, both SEM and profilometry failed to reveal any significant microstructural-level damage resulting from these large macroscopic changes even in the presence of very sharp cracks (Fig. 7). This demonstrates that the electrolyte layer has far more compliance than was previously anticipated. The quantitative data from profilometry (Fig. 8) was able to reveal the overall curvature changes, an additional advantage of the surface profilometer as a manufacturing diagnostic tool.

4.2 Crack types and morphology via profilometry

By comparing the initial morphology of the cracks in the electrolyte layer with those found in the non-fuel cell literature [8, 9], we can conclude that both larger cracks due to sintering or cosintering mismatches (Fig. 5 (a, c)) and fine ‘channeling’ cracks due to thermal mismatch (Fig. 5 (c)) were detected. Profilometry can obviously detect cracks that have substantially larger crack separations. It also shows that the edges of these cracks are elevated above the surrounding electrolyte consistent with the fact that this coating experiences compressive stress resulting from non-optimal shrinkage of the anode layer. Although SEM can detect finer cracks, profilometry can provide statistically valid

information (distribution, morphology and location) regarding the large cracks likely to lead to mechanical and electrochemical failure in a completely non-destructive manner.

4.3 Crack density and curvature

Interestingly, following reduction the curvature of specimens A and B are similar (Fig. 8 (a, b)) even though they were sintered at different temperatures. The curvature evolution of specimen C is markedly different from that of A and B, especially following reduction at 600°C. Crack density in the electrolyte following sintering may be responsible. Figs. 2 and 3 clearly show that cracks in the electrolyte surfaces of A and B are part of a crack network while those in C are more widely scattered. In addition, the crack densities in A and B are much higher than in C. Therefore, it is reasonable to infer that the interfacial strength between the electrolyte and the anode substrate in specimen C was stronger than that in specimens A and B. The constraint of the electrolyte layer by the substrate in A and B would be much smaller than that in C when the substrate shrank due to the reduction of NiO to Ni. This likely resulted in smaller increases in curvature following reduction at 600°C.

The most dramatic consequence of this becomes obvious following the rapid oxidation of the reduced specimens: the curvature of samples A and B increased substantially while that of C remained almost unchanged. This is contrary to the commonly accepted idea that oxidation causes expansion in the anode substrate [11] and should reverse the curvature observed following reduction. This phenomenon is probably due to the combined effects of both delamination and oxidation. The delamination in specimen C is likely contained within the anode due to the stronger bonding between the electrolyte and the top layer of the anode. In addition, the oxidative expansion was released by the electrolyte cracking

and, therefore, specimen C exhibits little visible change in curvature following oxidation (Fig. 8 (c)). On the other hand, the electrolyte-substrate bonding of specimen A is weaker. Following oxidation the effects of the delamination in the anode substrate can transfer to the top surface and lead to significant surface curvature change (Fig. 8 (a)). In addition, nonuniform oxidation in these laminates could also conceivably contribute to the curvature changes [12] . Carefully designed experiments are needed to further test this hypothesis.

5. Conclusions

Non-contact profilometry can detect sintering cracks nondestructively and provide quantitative data regarding curvature changes before and after sintering, reduction and reoxidation. The cracked areas of the electrolyte surface are flatter than those uncracked regions. NiO reduction results in increases in curvature. Initial crack density affects curvature evolution during reduction; the higher the crack density, the smaller the curvature increase following reduction at 600°C.

REFERENCE

- [1] R. K. Bordia, R. Raj, J. Am. Ceram. Soc., 68 (1985) 287-292.
- [2] A. G. Evans, J. W. Hutchinson, Acta. Metall. Mater., 43 (1995) 2507-2530.
- [3] C. Hillman, Z. Suo, F. F. Lange, J. Am. Ceram. Soc., 79 (1996) 2127-2133.
- [4] H. Tomaszewski, H. Weglarz, M. Boniecki, W. M. Recko, J. Mater. Sci., 35 (2000) 4165-4176.
- [5] R. Okuyama, E. Nomura, J. Ceram. Soc. Japan, 101 (1993) 1001-1005.
- [6] T. Garino, Ceramic engineering and Science Proceedings, 23 (2002) 759-765.
- [7] S. Majumdar, T. Claar, B. Flandermeyer, J. Am. Ceram. Soc., 69 (1986) 628-633.

- [8] B. F. Sørensen, S. Primdahl, J. Mater. Sci., 33 (1998) 5291-5300.
- [9] P. Z. Cai, D. J. Green, G. L. Messing, J. Am. Ceram. Soc., 80 (1997) 1929-1939.
- [10] A. Selcuk, G. Merere, A. Atkinson, J. Mater. Sci., 36 (2001) 1173-1182.
- [11] M. Mori, T. Yamamoto, H. Itoh, H. Inaba, H. Tagawa, J. Electrochem. Soc., 145 (1998) 1374-1381.
- [12] G. Stathis, D. Simwonis, F. Tietz, A. Moropoulou, A. Naoumides, J. Mater. Res., 17 (2002) 951-958.

List of captions

Fig. 1. Profilometry images of specimens sintered at various temperatures. (a) Specimen A sintered at 1400°C, (b) specimen B sintered at 1350°C and (c) specimen C sintered at 1350°C. The color bar provides a scale revealing the variation in surface height.

Fig. 2. Profilometry images with curvature removed taken from specimens (a) A, (b) B and (c) C. The failures in the electrolyte coating are indicated.

Fig. 3. Profilometry images of selected areas from specimens (a) A, (b) B and (c) C. The schematics show the location of the selected areas in the corresponding specimen.

Fig. 4. Curvature versus crack density in the coating of specimens (a) A, (b) B and (c) C.

HD: high crack density, LD: low crack density, none: no cracking, +: crack.

Fig. 5. Comparison between SEM and profilometry of the cracked coating surface in the as-sintered specimens; (a) cracked area, (b) uncracked area and (c) small cracks.

Fig. 6. Gravimetric behavior of anode specimens following reduction at 600°C, 750°C and oxidation at 750°C, respectively. 'G0' is the initial weight of the as sintered specimens.

Fig. 7. Comparison of surface morphology between SEM and profilometry post reduction at 600°C. (a) SEM and (b) profilometric morphologies of the same zone in Fig. 5 (a) after reduction and (c) SEM of the same zone in Fig. 5(c).

Fig. 8. Comparison of curvature along same diameter before and after reduction/oxidation for specimens (a) A, (b) B and (c) C.

Fig. 9 Curvature in specimen A, B and C across the center following oxidation at 750°C

Fig. 10. SEM surface morphology before and after oxidation at 750°C. (a) specimen A post reduction at 600°C; (b) same area in (a) post oxidation; (c) specimen C post reduction at

600°C; (d) same area in (c) post oxidation. New channeling cracks developed in both the electrolyte and the anode.

Deleted: <sp>

Fig. 1. Profilometry images of specimens sintered at various temperatures. (a) Specimen A sintered at 1400°C, (b) specimen B sintered at 1350°C and (c) specimen C sintered at 1350°C. The color bar provides a scale revealing the variation in surface height.

Fig. 2. Profilometry images with curvature removed taken from specimens (a) A, (b) B and (c) C. The failures in the electrolyte coating are indicated.

Fig. 3. Profilometry images of selected areas from specimens (a) A, (b) B and (c) C. The schematics show the location of the selected areas in the corresponding specimen.

(a)

(b)

Fig. 4. Curvature versus crack density in the coating of specimens (a) A, (b) B and (c) C.

HD: high crack density, LD: low crack density, none: no cracking, +: crack.

SEM

profilometry

(a)

SEM

profilometry

(b)

SEM

profilometry

(c)

Fig. 5. Comparison between SEM and profilometry of the cracked coating surface in the as-sintered specimens; (a) cracked area, (b) uncracked area and (c) small cracks.

Fig. 6. Gravimetric behavior of anode specimens following reduction at 600°C, 750°C and oxidation at 750°C, respectively. 'G0' is the initial weight of the as sintered specimens.

Fig. 7. Comparison of surface morphology between SEM and profilometry post reduction at 600°C. (a) SEM and (b) profilometric morphologies of the same zone in Fig. 5 (a) after reduction and (c) SEM of the same zone in Fig. 5(c).

(a)

(b)

(c)

Fig. 8. Comparison of curvature along same diameter before and after reduction/oxidation for specimens (a) A, (b) B and (c) C.

Fig. 9 Curvature in specimen A, B and C across the center following oxidation at 750°C

(a)

(b)

(c)

(d)

Fig. 10. SEM surface morphology before and after oxidation at 750°C. (a) specimen A post reduction at 600°C; (b) same area in (a) post oxidation; (c) specimen C post reduction at 600°C; (d) same area in (c) post oxidation. New channeling cracks developed in both the electrolyte and the anode.

Effects of reduction process parameters on the microstructure and mechanical properties of NiO/YSZ anodes.

Yaou Wang, Mark E. Walter
Department of Mechanical Engineering
The Ohio State University

Matthew Seabaugh, Katarzyna Sabolsky
NexTech Materials, Ltd

Abstract

Before solid oxide fuel cells with NiO/YSZ anodes begin to operate, a reduction reaction converts the NiO to Ni and forms network of pores. During actual operation, the reduction operation may continue on a smaller scale. As a result of the reduction reaction, the mechanical properties of the anode will change and may affect the stability of the whole membrane. In this research, the effects of reduction process parameters on mechanical properties of NiO/YSZ anode are studied. In particular, one reduction method involved introducing forming gas at room temperature and holding for 2 hours at 600° C while the other method introduced forming gas only after the specimen reached 600° C. Concentric ring-on-ring bi-axial flexure experiments were used to measure the strength. The results showed that for specimens that had been reduced more, there was an obvious trend of decreasing strength, increasing porosity, and decreasing Young's modulus. The temperature at which forming gas is introduced has a strong effect on the microstructure and thus also on the mechanical properties. Introducing forming gas at room temperature caused a poorly connected microstructure and significantly weakened the specimens. Thus reduction at a constant temperature is recommended for the NiO/YSZ anode.

1. Introduction

Although currently there is tremendous interest in fuel cells, there is still much work to be done before fuel cells can solve the world's power generation needs in a commercially viable and sustainable manner. Although there are many types of fuel cells, the basic operating principle remains the same: electrodes and proton or ion conducting membranes convert the chemical energy in a fuel directly to useable electrical energy. At 700-1000° C, the Solid Oxide Fuel Cell's (SOFC's) higher operating temperature allows H₂/CO to be oxidized directly at the anode. Thus the SOFC is compositionally simpler and has higher efficiency [1]. It is generally thought that the SOFCs high operating temperature restricts SOFCs to small and large scale stationary power applications or to small scale auxiliary power units for transportation [1, 2]. In order to eliminate sealing problems, SOFCs with the highest operating temperatures (~950°C) are typically manufactured in a tubular design. However, tubular designs are expensive to fabrication, and the power density is not ideal. [1]. Therefore, the current thrust in SOFC manufacturing is to make smaller planar cells that operate at 500-600°C. The lower operating temperature would make this SOFC applicable for auxiliary power units in transportation and the issues surrounding seals of the cell are more tractable [2]. Questions surrounding the durability of SOFCs remain to be investigated.

A single planar SOFC is a solid-state device consisting of two porous electrodes isolated by a dense oxygen ion conducting electrolyte. In anode-supported SOFCs, the anode and electrolyte are manufactured as one laminate. Although electrolyte-supported SOFCs exist, the

anode-supported designs allow lower operating temperature and thus will decrease the cost and improve the performance [3]. Many studies have been done on identifying and optimizing the functional performance of the materials used in SOFCs. Yttria Stabilized Zirconia (YSZ) is the most widely used electrolyte material. Anode materials require high electric conductivity, thermodynamic stability as well as physical and chemical compatibility with other cell components [4]. The most popular anode material is a Ni/YSZ porous cermet, which is originally sintered as NiO/YSZ and is then reduced to the Ni/YSZ cermet [4, 5]. When assembled and used, SOFCs membrane electrode assemblies (MEAs) fail from residual stresses, assembly stresses, thermal cycling, reduction and oxidation reactions, and intrinsic operational stresses. Study of mechanical properties of SOFCs will enable quantification of stresses and material degradation, and is required to understand reliability issues.

Some studies have reported results for mechanical properties of SOFC membranes. The residual stresses in the laminate at room temperature result primarily from the thermal expansion mismatch between the anode and electrolyte [6, 7]. Young's modulus and Poisson's ratio, as well as their relationship with temperature and porosity, of the anode and electrolyte materials have been characterized [8]. Flexural strength of electrolytes and laminates at both room temperature and elevated temperature has been determined with ring-on-ring experiments [9-13]. Fracture toughness of the electrolyte was measured by indentation fracture and double torsion loading methods [9, 13]. Plastic behavior of Ni/YSZ anode and the supported YSZ electrolyte was characterized by high temperature (1000-1200°C) tensile experiments [14]. However, limited studies have been done on the properties resulting from the reduction of NiO/YSZ to

Ni/YSZ. The effects of temperature and YSZ weight percent on the reduction behavior of NiO and microstructure of the products were investigated [15, 16]. Damage to YSZ electrolyte due to the reoxidation of Ni was also studied [17]. For the anode supported laminate, the effect of reduction on the mechanical properties of the anode is important for overall reliability. In this paper, the changes of mechanical properties of NiO/YSZ anode due to reduction will be investigated. The fracture caused by ring-on-ring loading will be studied. Strength, elastic modulus, and microstructure changes will be characterized and related to each other.

2. Experiments:

2.1 Samples and their reduction:

The disc shaped NiO-Y₂O₃ anode laminates were supplied by NexTech Ltd. The specimens were prepared by tape casting, and the sintered laminates were about 500 µm thick and 25.4 mm in diameter. The surface profile was measured with an optical profilometer on randomly chosen specimens. It was found that the departure from surface flatness within the bending region radius of 16 mm was less than 50µm.

Reduction of NiO/YSZ was performed in a forming gas mixture of 5% H₂ and 95% N₂ in a tube furnace. The maximum reduction temperature was chosen to be 600°C. Two reduction conditions were studied:

Method 1 involved heating the specimens from room temperature to 600°C at a rate of 2°C/min and holding the temperature at 600°C for 2 hours, with gas mixture flowing from the beginning of heating at a rate of 2000 sccm (standard cubic centimeter) until specimen was cooled to room temperature;

Method 2 was the same as Method 1 except that the forming gas was not added until the temperature reached 600°C. Different reduction fractions for Method 2 were achieved by controlling the holding time at 600°C for 2, 4 and 7 hours.

For both methods, the reduction time was calculated from the beginning of gas mixture flow to the end of holding temperature at 600°C. Hence the reduction time for Method 1 was 7 hours. The reduction fraction was characterized by measuring the mass lost.

2.2 Equibiaxial flexural strength test:

The equibiaxial flexural strength was measured with concentric ring-on-ring bending experiment at room temperature. The concentric ring-on-ring loading method eliminates the effects of the edge defects on the perimeter of specimens. This is a significant benefit since the edge defects are very common in ceramics and cause large scatter in data from uniaxial bending and tension experiments. In addition, in actual operation the thermal expansion mismatch between the anode and electrolyte creates a biaxial stress state in the laminate.

Figure 1 shows a schematic of the concentric ring-on-ring loading configuration, which was designed according to ASTM standard C1499 [18]. The specimen disc was placed concentrically between the loading ring and the support ring. The diameters of loading ring (D_L) and support ring (D_S) are 6.35mm and 15.875mm, respectively. The curved sections of the loading and support rings that would touch the sample had a radius of approximately 1mm in diameter. Teflon tape was placed between the loading ring and the compressive surface of specimen to minimize friction. A piece of 250 μ m thick rubber was put between the support ring and the tension surface of the specimen to minimize the effects of specimen-ring misalignment. Load was applied to the specimen through displacement (2.54 μ m/sec) of both the loading ring and support ring. The ball enabled the load ring to tilt in order to accommodate misalignment of fixturing and/or specimens. The load cell measured force directly.

The equibiaxial flexural strength σ_f from ring-on-ring loading can be calculated by the following equation [18]:

$$\sigma_f = \frac{3F}{2\pi t^2} \left[(1-\nu) \frac{D_s^2 - D_L^2}{2D^2} + (1+\nu) \ln \frac{D_s}{D_L} \right] \quad (1)$$

where t is the specimen thickness, D is the specimen diameter, ν is Poisson's ratio, and F is the measured force. Equation (1) is valid only when the deflection of specimen is small in comparison with the specimen thickness t . The maximum deflection δ of each specimen (occurs in the center) can be calculated by [18]:

$$\delta = \frac{3F(1-\nu^2)D_L^2}{8\pi Et^3} \left(\frac{D_s^2}{D_L^2} \left[1 + \frac{(1-\nu)(D_s^2 - D_L^2)}{2(1+\nu)D^2} \right] - \left(1 + \ln \frac{D_s}{D_L} \right) \right) \quad (2)$$

where E is Young's Modulus of the material.

2.3 Verification of the ring-on-ring loading design:

Equations (1) and (2) are developed from plate theory [19]. In order to ensure plate theory is valid for describing the ring-on-ring loading experiment, it is typically required that $D_s \geq 10t$, $D - D_s \geq 2t$, $t/\delta > 2$, and the radius of deflection curve must be much bigger than the thickness [18, 20]. The first two criteria were satisfied by proper design of the fixture. Equation (2) and finite element simulations were taken to study the thickness to deflection ratio requirement. The elastic constants were chosen, according to published data [7, 11], as $E=80\text{GPa}$, $\nu=0.31$, $\sigma_f=130\text{MPa}$. Dimension of samples were $D=25\text{mm}$ and $t=500\mu\text{m}$. The deflection δ calculated by Equations (1) and (2) was $110\mu\text{m}$, so that $t/\delta=4.5$. Hence the third requirement was also satisfied. However, since stress concentrations under the loading ring for $t/\delta < 10$ can cause fracture to initiation under the loading ring [20], the stress distribution near the loading ring needed to be considered.

Abaqus finite element software was used to simulate the ring-on-ring loading experiment. An axisymmetric planar shell model of a specimen disc with a 0.5mm thickness and a 12.5mm radius was set up, as shown in **Figure 2**. The radius of the tips of the loading and support rings were both 0.5mm. In order to reduce the effect of non-linear geometry, nonlinear loading step was used. A displacement of 85μm was added to the loading ring and the results are plotted in **Figure 3**. The center deflection was 107μm, which was very close to theoretically calculated value for the maximum deflection. The maximum strength of 133.8 MPa occurred within the loading circle. The distribution of strength within the loading circle was very uniform with a variation of strength of less than 0.83%. Thus reasonable breaking patterns could be expected from this design.

The last requirement, that radius of deflection curve be much bigger than the thickness, was also studied with finite element simulations. The deformed deflection curve was fitted by an eight degree polynomial $y=f(x)$, shown as black curve in **Figure 3** (a). The radius ρ in any point x can be defined mathematically as:

$$\rho(x) = \left| \frac{\left(1 + (y')^2\right)^{3/2}}{y''} \right| \quad (3)$$

where $(g)'$ represents differentiation with respect to x . In this case, the minimum radius ρ_{min} occurs in the center of the disc with a value of 140mm, which is much bigger than the thickness $t=0.5\text{mm}$.

2.4 Elastic modulus:

The Young's moduli were measured at room temperature through uniaxial tension experiments. **Figure 4** shows the schematic for the uniaxial experiments. The rectangular shaped specimens approximately 4mm wide and 25mm long were cut from the circular discs using a slow-cut diamond saw. The specimen was glued to the grips using a custom alignment fixture and Loctite 401. Loading was performed using the same apparatus used for the ring-on-ring experiment. Strain was measured using a strain gage.

2.5 Microstructure:

Microstructure was studied using SEM imaging. SEM micrographs were taken of the fracture surfaces and on polished cross sections. For polished surfaces, the surfaces were coarsely polished with sandpaper from 600 to 2000 grit, and then fine polished with diamond paste from 3000 to 50,000 grit. Specimens were randomly picked from each group. The porosity was measured by water immersion according to ASTM standard C20-00 [21]. An analytical balance with resolution down to 0.001g was used to determine specimen weight for reduction fraction calculations and for porosity measurements.

3. Results

3.1 Reduction fraction:

The average percentage of mass lost during reduction is shown in Table 1 for each reduction method. There is a big increase of mass lost for reduction Method 2 from 2 hours to 4 hours of reduction time. After 4 hours, mass lost became slow and less obvious. This means the reduction speed decreased as reduction was going on, and most reduction of NiO happened in the first 4 hours. When comparing the two methods with 7 hours of reduction time, the mass lost fraction of Method 1 is bigger than that of Method 2, and the reduction time of Method 1 includes the time spent at room temperature, which means a shorter actual reduction time. It is also noted that the variation of mass lost percentage of Method 1 is much wider than that of Method 2

3.2 Equibiaxial flexural strength:

The average, room temperature equibiaxial flexural strengths of specimens from each reduction method are shown in Table 1. The failure of ceramics is typically affected by defects and follows a statistical distribution. It is appropriate to employ a two parameter Weibull distribution to analyze the scatter in the biaxial strength data [22]:

$$\ln \left(\ln \left(\frac{1}{1 - P_f} \right) \right) = m \ln \sigma - m \ln \sigma_0 \quad (4)$$

where P_f is the Weibull distribution of failure probability, σ is the failure stress, m is the Weibull modulus, and σ_0 is the characteristic strength. The Weibull modulus describes the width of the strength distribution, with higher Weibull modulus values indicating lower strength variability.

Usually, the Weibull modulus of ceramics is in the range of 5-20. The characteristic strength locates the distribution in stress space and represents the strength of a body with effective volume at a failure probability of 0.632 [22]. If a batch contains n specimens, the specimens are ranked from 1 to n in increasing order of strength and the probability P_f of specimen i is calculated by [22]:

$$P_{f_i} = \frac{i - 0.5}{n} \quad (5)$$

After plotting $\ln\left(\ln\left(1/(1 - P_{f_i})\right)\right)$ versus $\ln \sigma_i$, the Weibull modulus m and characteristic strength σ_0 can be obtained from the slope and intercept, respectively, of a least squares fit of the data.

The Weibull plot of each reduction method is shown in **Figure 5** and the Weibull moduli and characteristic strengths are listed in Table 1. In comparison with previously reported data [12], a series of very good Weibull moduli, *i.e.*, relatively small variability in strength, were achieved from the experiments. This shows that the specimens have a more consistent microstructure. For both reduction methods, the average strength and characteristic strength both decreased as the fraction of reduced NiO increases. The Weibull modulus of Method 1 became smaller after reduction, while that of Method 2 increased. Accordingly, the variability in strength from Method 1 was larger than that for Method 2.

3.3 Breaking patterns:

A photograph showing representative breaking patterns is shown in **Figure 6**. To more accurately characterize breaking patterns, purple dye was painted on the Teflon tape before loading. The dye was transferred to the specimens during loading and breaking patterns could

be examined with respect to the loading ring locations. It is very obvious to see that the fractures initiated within the loading circles, verifying the validity of the ring-on-ring apparatus. The unreduced samples usually broke into several small pieces; for both methods, the reduced samples seldom broke to more than four parts. Comparison of the broken pieces with the corresponding strength matches the breaking pattern descriptions in ASTM Standard 1499 [18]. More broken pieces correspond to higher fracture strength. For Method 2, some samples did not even fail in a brittle fashion and remained intact after losing load carrying capability.

3.4 Elastic modulus:

The average elastic modulus of specimens of each group is shown in Table 1. The Young's modulus decreased after reduction for both methods. The decreasing in Young's modulus of Method 1 was faster than that of Method 2. For Method 2, the Young's modulus decreased as the NiO reduction fraction increased.

3.5 Porosity

The porosity is shown in Table 1. For both methods, after reduction, the porosity had increased. For Method 2 the porosity continued to increase with increasing reduction time. Because of the wide variation of porosity for Method 1, it is difficult to discern a difference in porosity between two reduction methods from Table 1. However, it can be seen in **Figure 7**, that when porosity is plotted versus mass lost percentage for each reduction method, the points associated with Method 2 are all above those of Method 1. Thus the porosity of Method 1 is

smaller than that of Method 2, which is the same conclusion reached when comparing the average porosity in Table 1.

3.6 SEM images:

SEM was used to characterize the microstructure before and after reduction. The secondary electron and backscattered electron images of polished cross section surfaces for each reduction method are shown in **Figure 8** and **Figure 9**. Fracture surface micrographs are shown in **Figure 10**. As seen in **Figure 9(b)**, in the backscattered electron images, the darker particles are higher atomic number (Ni or NiO), while the lighter areas are YSZ.

Comparing the photos between the unreduced and reduced samples in **Figure 8**, it can be seen that size of the large pores does not change noticeably, but many new, tiny pores are formed during reduction. These small pores are also found throughout **Figure 9** and **Figure 10**. Reduction of NiO also caused a decrease in the Ni particle size, which can be seen in **Figure 10**. As a result with increased pore density, it becomes easier for damage to propagate through the reduced specimens. In unreduced specimens grains that have been cleaved by the fracture process can be found and are marked with circles in **Figure 10** (a) and (b).

When comparing images from different reduction methods in **Figure 8-Figure 10**, there are no obvious differences in the pore size and number. However, it is clear from **Figure 9**.that Method 1 produces Ni and NiO particles that are smaller than those in Method 2. There is no apparent change in pore size, pore number, and particle size for Method 2 with different reduction times.

4. Discussion

4.1 Reduction:

By comparing the percentage of mass lost during reduction, it has been found that Method 1 had a more complete reduction in a shorter period of time compared to Method 2. The differences are significant. The only difference between Method 1 and Method 2 involves the temperature at which forming gas is introduced. In Method 1 forming gas is introduced at room temperature. The gas then has time to infiltrate the whole specimen before reduction reactions take place. Once the temperature reaches the activation temperature for the reduction reaction, the reaction will take place throughout the sample. On the other hand, for Method 2, forming gas is introduced at high temperature, and therefore the reduction reaction begins at the surface where the forming gas first contacts the NiO. In Method 2 the reduction proceeds more slowly into the interior of the specimen.

Secondly, as temperature went up, the particles of NiO/Ni and YSZ would both expand. Thus there would be a stronger interaction between YSZ particles and newly reduced Ni particles than the reduction at constant temperature. This made it more difficult to form big Ni particles, which can be observed in **Figure 9**, where size of Ni/NiO particles of Method 1 is smaller than that of Method 2. This supplied more contacting area for reducing gas. Meanwhile, many very tiny pores should be expected to occur in the junction of YSZ and Ni/NiO particles, which would compose possible path for reducing gas. The effect of more small pores is to let Method 1 keep more NiO in contact with reducing gas as compared to Method 2.

Before using these two differences to explain the bigger mass lost percentage of Method 1, an assumption is needed. From the reduction fraction results in Sec. 3.1, it has been observed that most reduction of NiO happened in the first 4 hours for Method 2. Accordingly, it will be assumed that most reduction happened in the first 4 hours for both methods. That means that mass lost percentage would be determined by the first 4 hours of reduction, called as effective reduction time in the following part. Now, the bigger mass lost percentage of Method 1 can be explained as: From the beginning of reduction, Method 1 kept a faster reduction speed than Method 2, and the effective reduction time of Method 1 was close to that of Method 2, so Method 1 lost more mass.

4.2 Equibiaxial flexural strength:

As shown in Table 1, when the reduction fraction of NiO increases, the strength from both methods decreases. Although one might expect the conversion of NiO to Ni would make a stronger material, the opposite is true: reduction reduces the strength of the anode. This strength reduction is believed to be the result of increased porosity which weakens the microstructure and the interfaces between Ni/NiO and YSZ particles. From SEM micrographs described in Sec. 3.6, it is observed that reduction of NiO caused many tiny pores among particles. These pores enable damage to propagate more easily. Because unreduced specimens had fewer tiny pores, damage needed to pass through some of the particles. The cleaved particles are highlighted in **Figure 10** (a) and (b). No such features were observed in reduced specimens.

The strength of specimens reduced with Method 1 is significantly less than the strength from

Method 2 specimens. It is reasonable to assume that the initiation of damage is the same for both methods. Thus the differences in strength are most likely due to the difference sized of Ni/NiO particles. As seen in **Figure 9**, the size of Ni/NiO particles of Method 1 is smaller than that of Method 2. It is easier for cracks to go around the smaller particles.

Statistically, as compared to unreduced samples, Method 1 reductions lowered the Weibull modulus (widened the strength variability) significantly, while Method 2 increased the modulus slightly (narrowed the variability). Because the variability in strength is usually affected by defects, it is thought that a more consistent microstructure is produced by Method 2. The less consistent properties of Method 1 are also reflected by the wider variation in mass lost percentage, shown in Table 1.

4.3 Elastic modulus and porosity:

Elastic modulus of ceramics is usually mainly affected by porosity. When comparing the elastic modulus with porosity between reduced and unreduced specimens, and among specimens of Method 2 with different reduction times, it can be observed that higher elastic modulus corresponds to smaller porosity. However, the opposite trend is observed when comparing the data of Method 1 with that of Method 2. In order to explain the bigger mass lost percentage and smaller tested porosity of Method 1, two possibilities are considered: First, the actual porosity of Method 1 is not bigger than that of Method 2, but the density of Ni particles of Method 1 is smaller than that of Method 2. This is less likely, because the initial densities of NiO are the same and the reduction procedure is not supposed to change the density of Ni particles.

Secondly, the densities of Ni particles of both methods are the same, but the measured porosity of Method 1 is not accurate. It has been observed that there are many tiny pores in Method 1 samples. It is possible that the water used in the porosity measurement [21] is not able to penetrate into these tiny pores, and therefore the measured porosity does not reflect the actual porosity.

5. Summary

Reduction of NiO/YSZ to Ni/YSZ changes the microstructure and effects mechanical properties. From this research, it has also been found that the temperature at which the reducing gas is added influences the microstructure and mechanical properties. In particular, the following observations have been made:

1. Reduction caused many tiny pores, weakening the structure and reducing the elastic modulus;
2. Reduction Method 1 had a faster reduction speed than reduction Method 2;
3. Compared to Method 2, Method 1 resulted in a weaker structure with smaller Ni/NiO particles, and accordingly a smaller elastic modulus and fracture strength;
4. Compared to the unreduced specimens, reduction Method 1 decreased the consistency of the results, giving a more scattered strength variation. Reduction Method 2 increased the consistency and gave a narrower strength variation.

These results indicate that when reducing the discs of NiO/YSZ, reducing gas should be introduced only after the reduction temperature is reached.

Acknowledgements

This work was supported by the National Science Foundation, (Grant: CMS-9984837; Program Manager: Dr. Jorn Larsen-Basse and Dr. Yip-Wah Chung). NexTech is gratefully acknowledged for providing samples and for many helpful discussions. The authors also wish to thank Professor John Lannutti and Dr. Wenxia Li for their help.

Bibliography

1. B.C.H. Steele, A.H., *Materials for fuel-cell technologies*. Nature, 2001. **414**: p. 345-352.
2. Haile, S.M., *Fuel cell materials and components*. Acta Materialia, 2003. **51**: p. 5981-6000.
3. A.V. Virkar, J.C., C.W. Tanner and J.W. Kim, *The role of electrode microstructure on activation and concentration polarizations in solid oxide fuel cells*. Solid State Ionics, 2000. **131**: p. 189.
4. W.Z. Zhu, S.C.D., *A review on the status of anode materials for solid oxide fuel cells*. Materials Science and Engineering, 2003. **A362**: p. 228-239.
5. Ormerod, R.M., *Solid oxide fuel cell*. Chem. Soc. Rev., 2003. **32**: p. 17-28.
6. A. Selcuk, G.m., A. Atkinson, *The influence of electrodes on the strength of planar zirconia solid oxide fuel cells*. Journal of Materials Science, 2001. **36**: p. 1173-82.
7. A. Selcuk, A.A., *Residual stress and fracture of laminated ceramic membranes*. Acta Mater., 1999. **47**: p. 867-874.
8. A. Selcuk, A.A., *Elastic properties of ceramic oxides used in solid oxide fuel cells(SOFC)*. Journal of the European Ceramic Society, 1997. **17**: p. 1523-32.
9. A. Selcuk, A.A., *Strength and Toughness of Tape-Cast Yttria-Stabilized Zirconia*. J. Am. Ceram. Soc., 2000. **83** [8]: p. 2029-35.
10. F.L. Lowrie, R.D.R., *Room and high temperature failure mechanisms in solid oxide fuel cell electrolytes*. Journal of the European Ceramic Society, 2000. **20**: p. 751-760.
11. I. R. Gibson, G.P.D., J.T.S. Irvine, *Influence of yttria concentration upon electrical properties and susceptibility to ageing of yttria-stabilised zirconias*. Journal of the European Ceramic Society, 1998. **18**: p. 661-667.
12. A. Selcuk, A.A., *Mechanical behavior of ceramic oxygen ion-conducting membranes*. Solid State Ionics, 2000. **134**: p. 59-66.
13. G.A. Gogotsi, V.I.G., B.I. Ozerskii, A.D. Vasil'ev, and V.I. Korban, *Fracture toughness, strength, and other characteristics of yttria-stabilized zirconium ceramics*. Refractories and Industrial Ceramics, 2000. **14**: p. 7-8.
14. F. Gutierrez-Mora, J.M.R.a.J.L.R., *High-temperature mechanical properties of anode-supported bilayers*. Solid state Ionics, 2002. **149**: p. 177-184.
15. H. Mori, C.-J.W., J. Otomo, K. Eguchi and H. Takahashi, *Investigation of the interaction between NiO and yttria-stabilized zirconia (YSZ) in the NiO/YSZ composite by temperature-programmed reduction technique*. Applied Catalysis A: General, 2003. **245**(79-85).
16. M. Marinek, K.Z., J. Ma?ek, *Preparation of Ni-YSZ composite materials for solid oxide fuel cell anodes by the gel-precipitation method*. Journal of Power Sources, 2000. **86**: p. 383-389.

17. M. Cassidy, G.L., K. Kendall, *The reduction of nickel-zirconia cermet anodes and the effects on supported thin electrolytes*. Journal of Power Sources, 1996. **61**: p. 189-192.
18. *Standard test method for monotonic equibiaxial flexural strength of advanced ceramics at ambient temperature*. ASTM, 2001. **C1499-01**: p. 768-777.
19. S.P. Timoshenko, S.W.-K., *Theory of Plates and Shells*. 2nd ed. Engineering societies monographs. 1959, New York, NY: McGraw-Hill.
20. M.E.Manley, T.E., C. Vaucamps and D. Gailus, *Four point and biaxial flexure strength of PZT ceramics: A probabilistic approach*. Ceramic Engineering and Science proceedings, 1999. **20(4)**: p. 459-466.
21. *Standard test methods for apparent porosity, water absorption, apparent specific gravity and bulk density of burned refractory brick and shapes by boiling water*. ASTM, 2000. **C20-00**: p. 6-8.
22. Green, D.J., *An Introduction to the Mechanical Properties of Ceramics*. 1st ed. Cambridge solid state science series. 1998, Cambridge, United Kingdom: Cambridge University Press.

List of Figures

- Figure 1.** Schematic of the concentric ring-on-ring loading configuration
- Figure 2.** Axisymmetric loading model of ring-on-ring test simulated by ABAQUS
- Figure 3.** Result of FEM simulation of ring-on-ring bending
- Figure 4.** Schematic of uniaxial tension test
- Figure 5.** Weibull distribution of biaxial flexural strength
- Figure 6.** Breaking patterns of discs after ring-on-ring loading experiments
- Figure 7.** Porosity change with mass lost percentage
- Figure 8.** Secondary electron images of polished intersection surfaces
- Figure 9.** Backscattered electron images of polished intersection surface
- Figure 10.** SEM photos of fracture surfaces

Reduction method	unreduced	reduction Method 1	reduction Method 2		
Reduction time(hours)	0	7	2	4	7
Mass lost percentage(%)	0	11.4 (0.102-0.122)	8.9 (0.084-0.089)	10.8 (0.105-0.114)	10.8 (0.103-0.118)
Average strength (MPa) and 95% confident interval	145.2±24.3	95.0±26.1	142.0±38.5	133.9±18.2	132.4±20.8
Weibull characteristic strength (MPa)	150.7	100.5	150.7	138	137
Weibull modulus	13.1	8.3	8	16.4	14.7
Young's modulus (GPa)	75.9	44.7	71.4	69.5	59.4
Porosity (%)	21.3 (21.15-21.4)	33.0 (29.9-37.1)	32.15 (31.0-33.3)	33.95 (33.3-34.6)	34.3 (33.0-36.4)

Table 1 Mechanical properties of each batch of specimens

Figure 1. Schematic of the concentric ring-on-ring loading configuration

Figure 2. Axisymmetric loading model of ring-on-ring test simulated by ABAQUS

Figure 3. Result of FEM simulation of ring-on-ring bending

Figure 4. Schematic of uniaxial tension test

Figure 5. Weibull distribution of biaxial flexural strength

Figure 6. Breaking patterns of discs after ring-on-ring loading experiments

Figure 7. Porosity change with mass lost percentage

(a) unreduced specimen

(b) method 1 with 7 hours

(c) method 2 with 2 hours

(d) method 2 with 7 hours

Figure 8. Secondary electron images of polished intersection surfaces

(a) method 1 with 7 hours

(b) method 2 with 2 hours

(c) method 2 with 7 hours

(d) method 2 with 4 hours

Figure 9. Backscattered electron images of polished intersection surface

Figure 10. SEM photos of fracture surfaces.