U.S. DEPARTMENT OF ENERGY

TOPICAL REPORT

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

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Abstract

This report summarizes the results of Phase II of this program, *Low-Cost Manufacturing Of Multilayer Ceramic Fuel Cells*. The objective of the program is to develop advanced ceramic manufacturing technologies for making planar solid oxide fuel cell (SOFC) components that are more economical and reliable for a variety of applications. Phase II development work focused on three distinct manufacturing approaches (or tracks) for planar solid oxide fuel cell elements. Two development tracks, led by NexTech Materials and Oak Ridge National Laboratory, involved co-sintering of planar SOFC elements of cathode-supported and anode-supported variations. A third development track, led by the University of Missouri-Rolla, focused on a revolutionary approach for reducing operating temperature of SOFCs by using spin-coating to deposit ultra-thin, nano-crystalline YSZ electrolyte films. The work in Phase II was supported by characterization work at Ohio State University. The primary technical accomplishments within each of the three development tracks are summarized below:

- **Track 1.** NexTech's targeted manufacturing process for planar SOFC elements involves tape casting of porous electrode substrates, colloidal-spray deposition of YSZ electrolyte films, co-sintering of bi-layer elements, and screen printing of opposite electrode coatings. The bulk of NexTech's work focused on making cathode-supported elements, although the processes developed at NexTech also were applied to the fabrication of anode-supported cells. Primary accomplishments within this track are summarized below:
  - Scale up of lanthanum strontium manganite (LSM) cathode powder production process.
  - Development and scale-up of tape casting methods for cathode and anode substrates.
  - Development of automated ultrasonic-spray process for depositing YSZ films.
  - Successful co-sintering of flat bi-layer elements (both cathode and anode supported).
  - Development of anode and cathode screen-printing processes.
  - Demonstration of novel processes for composite cathode and cermet anode materials.

- **Track 2.** ORNL's development work focused solely on making anode-supported planar cells by tape casting of a porous anode substrate, screen printing of a YSZ electrolyte film, co-sintering of the bi-layer element, and screen-printing of an opposite cathode coating. Primary accomplishments within this track are summarized below:
  - Development and scale-up of anode tape casting and lamination processes.
  - Development of proprietary ink vehicle for screen-printing processes.
  - Development of screen-printing process for depositing YSZ films.
  - Successful co-sintering of flat bi-layer anode-supported elements.
  - Development of cathode screen-printing process.

- **Track 3.** UMR's process development work involved fabrication of a micro-porous cathode substrate, deposition of a nano-porous interlayer film, deposition of nano-crystalline YSZ electrolyte films from polymeric precursor solutions, and deposition of an anode coating. Primary accomplishments within this track are summarized below:
  - Development and scale up of tape casting and sintering methods for cathode substrates.
  - Deposition of nano-porous ceria interlayer films on cathode substrates.
  - Successful deposition of dense YSZ films on porous cathode substrates.
  - Identification of several anode material options.

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Introduction

This document describes the results of Phase II development work conducted under this DOE-funded program, *Low-Cost Manufacturing Of Multilayer Ceramic Fuel Cells*. The prime contractor is NexTech Materials, Ltd., and subcontractors include Adaptive Materials Inc., Advanced Materials Technologies, Edison Materials Technology Center, Gas Technology Institute, Iowa State University, Michael A. Cobb & Co., Northwestern University, Ohio State University, and University of Missouri-Rolla (UMR). Oak Ridge National Laboratory (ORNL) is supporting this program with separate DOE funding. The objective of the program is to develop advanced manufacturing technologies for making solid oxide fuel cell components that are more economical and reliable for a variety of applications.

In Phase I, stack manufacturing cost and development risk were assessed for five different solid oxide fuel cell (SOFC) design and fabrication approaches:

(1) Planar stacks of cathode-supported elements made using NexTech's proposed tape casting, colloidal spray deposition, co-sintering and screen printing methods (baseline program);

(2) Planar stacks of anode-supported elements made using ORNL's proposed tape casting, screen printing and co-sintering methods (baseline program);

(3) Planar stacks of cathode-supported elements made by UMR's proposed tape casting, spin-coating and screen printing methods (Option 1);

(4) Planar stacks of anode-supported planar elements made by co-extrusion and co-sintering methods, originally proposed by Adaptive Materials (Option 2); and

(5) Proprietary "monolithic" cell/stacks based on a design conceived by Michael A. Cobb & Co. (for comparison only).

Based on the results of this Phase I study, which were documented in a topical report dated October 23, 2000, 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 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 1. Technical challenges addressed by our work in Phase II are summarized in Table 1. 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. In this report, results of Phase II development work are summarized and discussed in the non-proprietary section that follows. Detailed descriptions of approaches and results of work performed at NexTech, ORNL and UMR are then provided within stand-alone proprietary appendices.

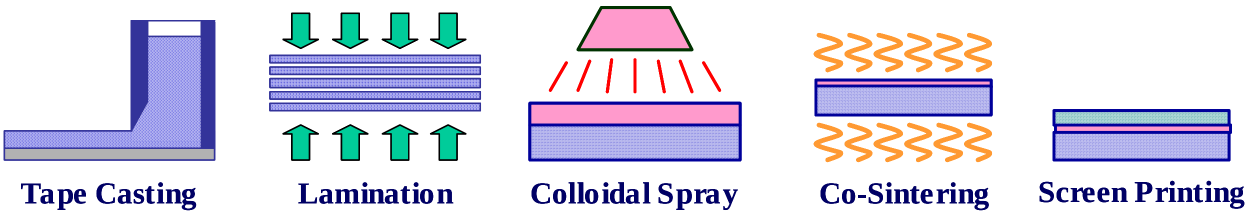

Figure 1a. Unit operations required for fabrication of planar, SOFC elements using the process developed by NexTech (Track 1).

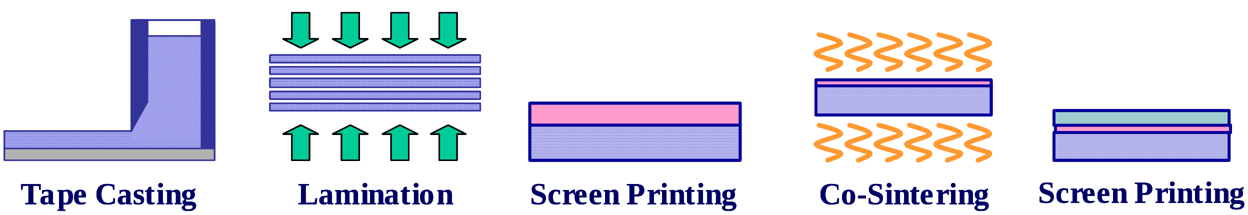

Figure 1b. Unit operations required for fabrication of planar, SOFC elements using the process developed by ORNL (Track 2).

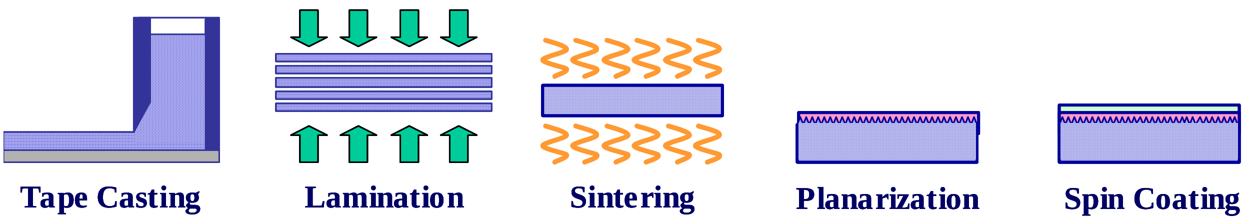

Figure 1c. Unit operations required for fabrication of planar, SOFC elements using the process developed by UMR (Track 3).

Table 1. 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.

Summary of Phase II Results

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 characterization by laser dilatometry and optical profilometry 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. The high level of collaboration in Phase II contributed greatly to the successful outcome of development efforts. The results of Phase II work at NexTech, Ohio State, ORNL and UMR are summarized below.

- Processes were 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 ten kilograms per week (see Figure 2). Characteristics of this LSM powder include a one-micron particle size and a surface area of 7-8 m^2/gram (see Figure 3). Electrical conductivities of dense LSM ceramic samples were similar to those obtained in the literature.

- Tape casting and lamination processes were developed at NexTech for porous LSM cathode and NiO/YSZ anode substrates. The porosity of sintered cathode and anode substrates was tailored by using suitable pore-forming fugitive materials. One of NexTech's strategies in substrate development was to maintain a high density of the skeletal ceramic phase within the porous LSM substrate, so that mechanical strength would be maximized (see Figure 4). The various process steps (tape casting, lamination, binder burnout, and sintering) were optimized to maintain flatness of sintered (or co-sintered) substrates.

- NexTech adapted a composite interlayer approach for the fabrication of cathode-supported electrolyte films. The two phases in the composite interlayer are gadolinium-doped ceria (GDC) and a perovskite electrode material that does not react with either YSZ or GDC. The interlayer composition was designed to prevent adverse reactions between the LSM cathode substrate and the YSZ electrolyte films during co-sintering and to improve low-temperature cathode performance. A spray deposition process was established for depositing these interlayer coatings (see Figure 5). These interlayer-coated LSM substrates also were used in conjunction with UMR's development work in Track 3.

- An improved process was established at NexTech Materials for the high yield and low cost production of dispersed nanoscale zirconia (YSZ) suspensions (see Figure 6). These aqueous suspensions are critical components of NexTech's colloidal spray deposition process for YSZ electrolyte films. 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 by conducting most of the fabrication work in a clean room (see Figure 7) and by using an automated ultrasonic spray deposition system that provides exceptional thickness uniformity of deposited films (see Figure 8).

- Co-sintering processes for cathode-supported and anode-supported electrolyte elements were established at NexTech. Co-sintered laminates had the desired morphology, with dense YSZ electrolyte films and porous electrode substrates (see Figures 9, 10, and 11). It should be noted that NexTech's initial process development work on anode-supported elements was performed in collaboration with ORNL (see Figure 10). NexTech's processes were scaled up for the fabrication of flat multilayer electrolyte elements with up to 50-cm^2 element areas.

- 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 in two dimensions during sintering, and supported the design of sintering cycles for cathode-supported elements. Optical profilometry provides a two-dimensional and quantitative measure of curvature in sintered laminates and co-sintered elements. LSM substrates produced during initial development work in Phase II exhibited considerable curvature, depending on the specific lamination conditions (see Figure 12). Optimization of processing conditions allowed the fabrication of sintered LSM laminates with flatness of less than 20 microns (see Figure 12). Optical profilometry also was used to characterize micron-scale surface topography (or roughness) of electrolyte elements during various stages of fabrication. An example is shown in Figure 14, which is a map of the surface of the same interlayer coating that was presented earlier (see Figure 5).

- ORNL developed tape casting and lamination methods for porous anode substrates, as well as screen-printing processes for depositing YSZ electrolyte films, and co-sintering methods for bi-layer electrolyte elements. 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. ORNL also developed processes for incorporating functional interlayers at the anode/electrolyte and cathode/electrolyte interfaces. ORNL's processes were scaled up to 100-cm^2 element areas. Details of ORNL's work are provided in Appendix B.

- 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 porous cathode substrates. UMR developed a method for infiltrating a lanthanum cobaltite (LSCF) electrode material into a nano-porous ceria interlayer – this composite interlayer is expected to provide good low-temperature cathode performance. UMR also established that nano-crystalline scandium-doped zirconia (ScZ) 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 the potential to be used as an anode interlayer to improve performance. Details of UMR's work are provided in Appendix C.

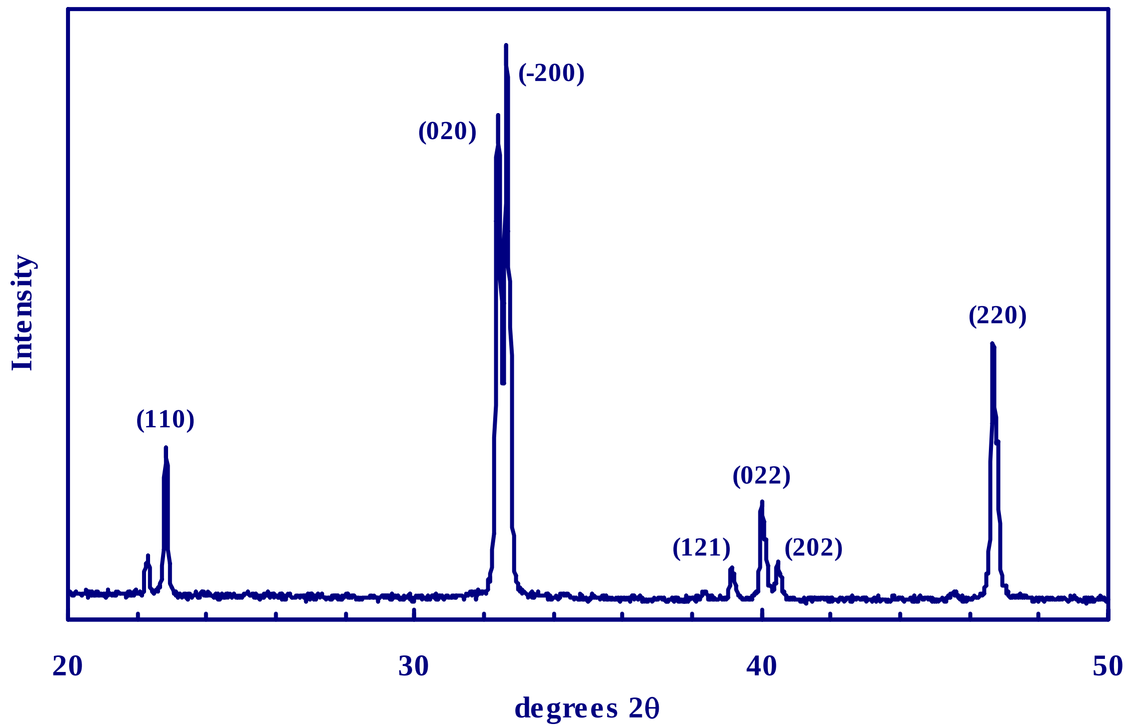

Figure 2. X-ray diffraction pattern of phase-pure lanthanum strontium manganite powder, produced by the process developed at NexTech in Phase II.

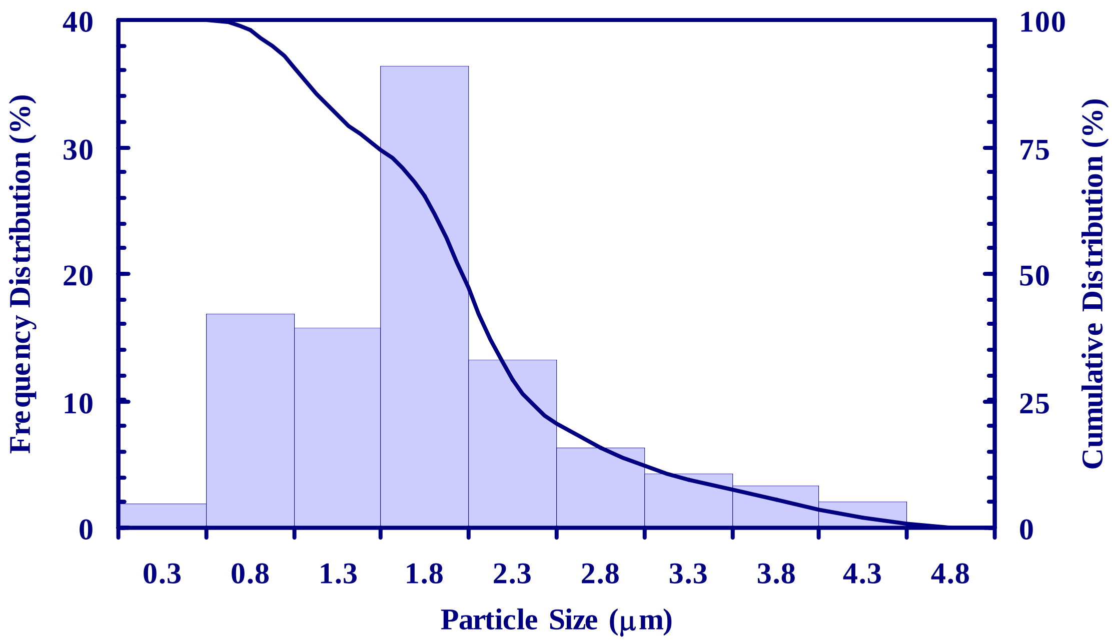

Figure 3. Particle size distribution of LSM powder, produced by the process developed at NexTech in Phase II.

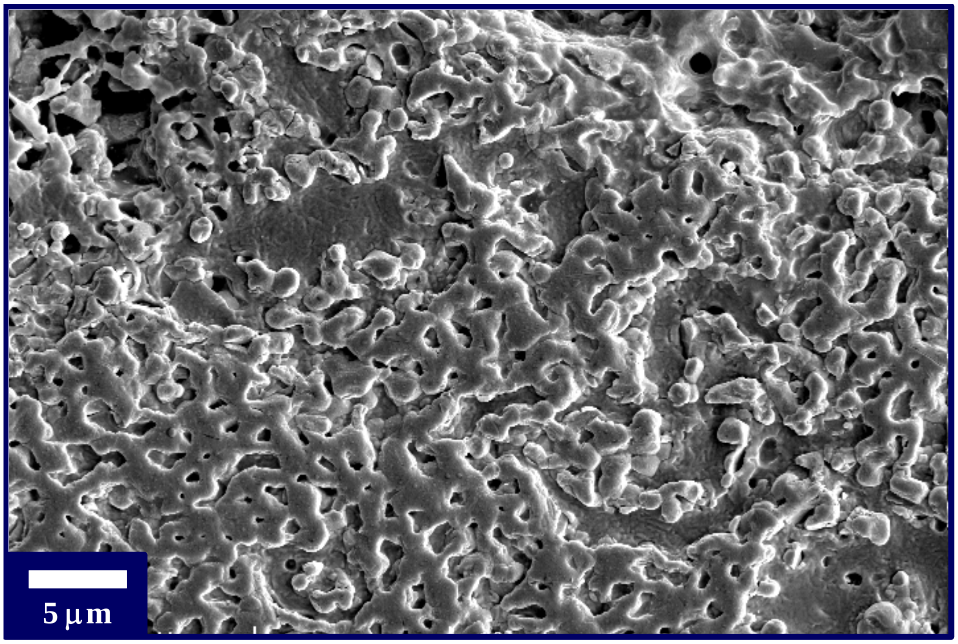

Figure 4. SEM micrograph of polished surface of porous LSM substrate prepared using optimized process and sintered at 1350ºC. Note the high density of the LSM skeletal structure.

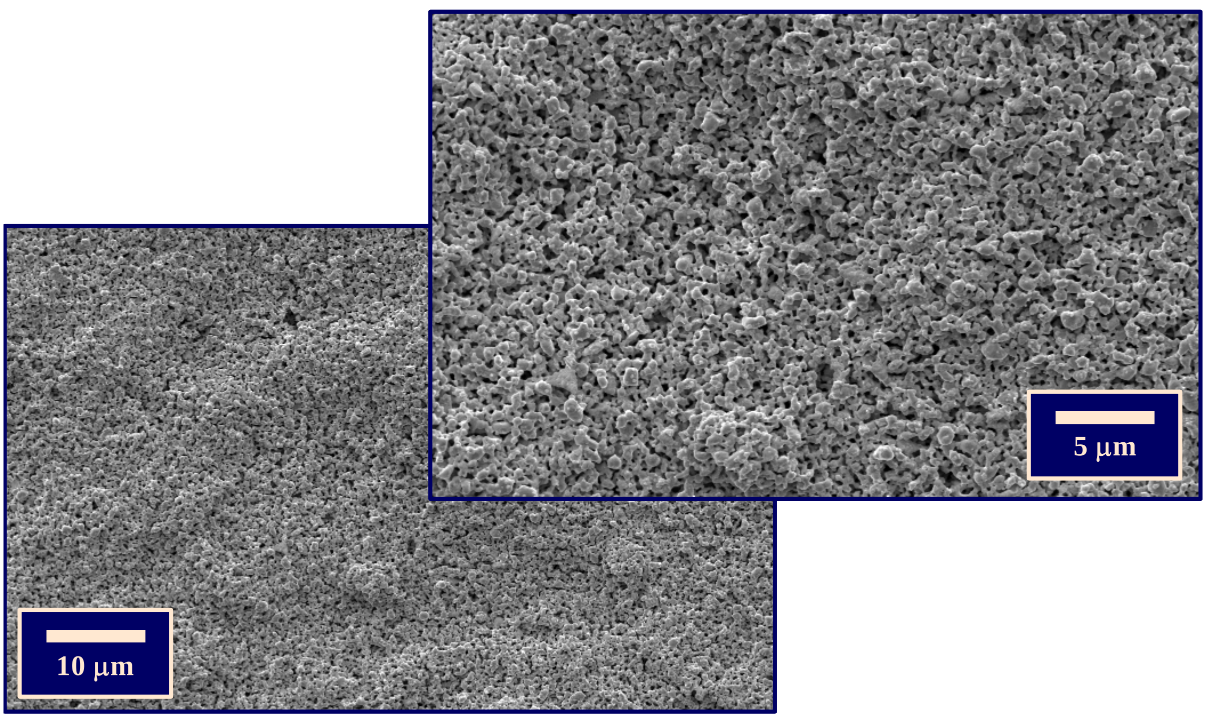

Figure 5. SEM micrographs of PSMF/GDC interlayer coating (deposited on an LSM substrate and sintered at 1300ºC.

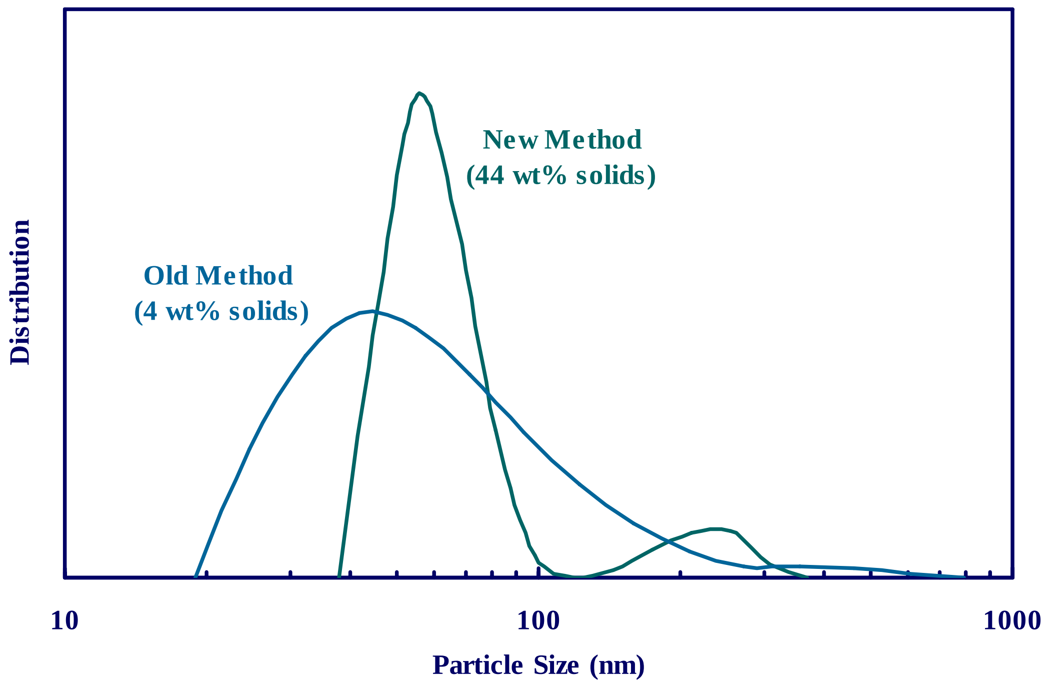

Figure 6. Particle size distributions of aqueous nanoscale YSZ suspensions produced at NexTech in Phase II. Note that the process developed by NexTech provides high solids content and narrow particle size distribution.

Figure 7. NexTech's multilayer ceramic fabrication clean-room facility.

Figure 8. Ultrasonic-spray deposition system used at NexTech for depositing YSZ electrolyte coatings.

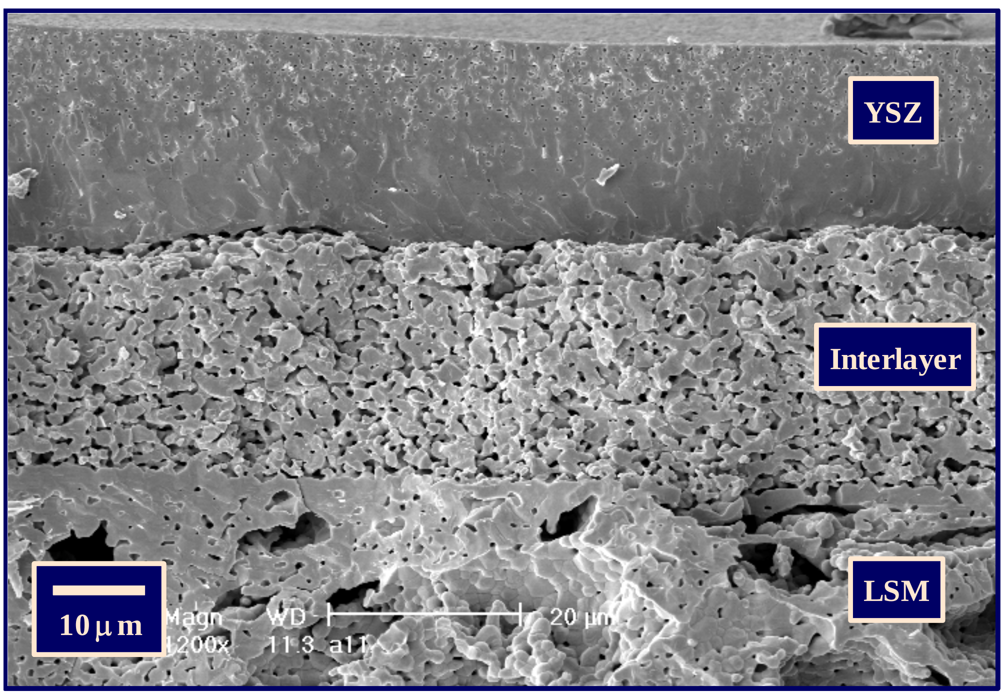

Figure 9. SEM micrograph of a fractured cross-section of a cathode-supported element. Note the micro-porous PSMF/GDC interlayer and high-density YSZ electrolyte films.

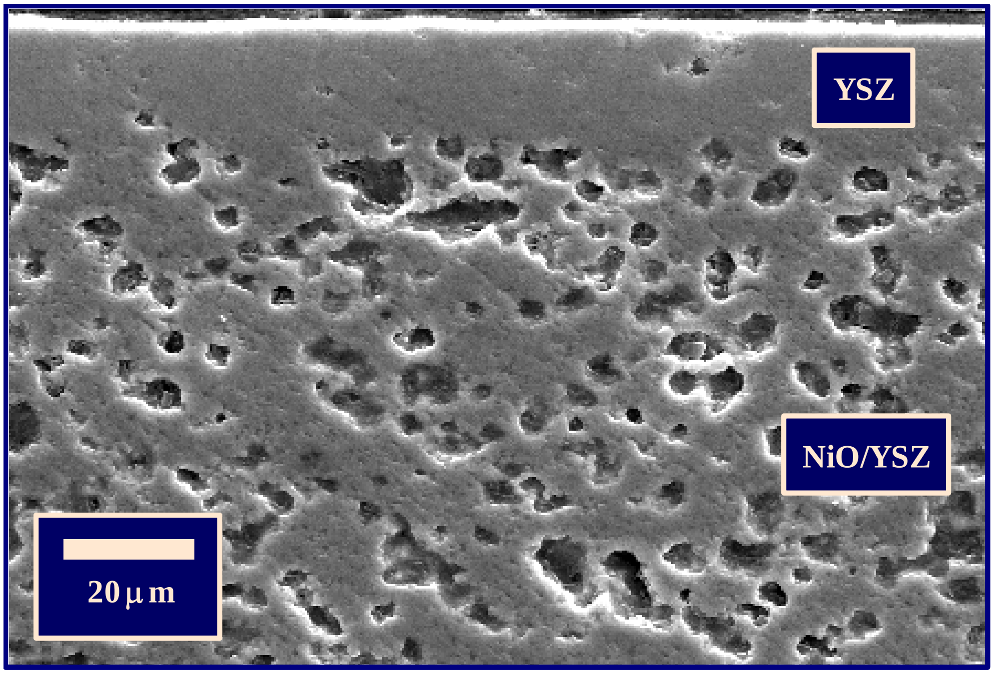

Figure 10. SEM micrograph of a polished cross-section of an anode-supported element. The NiO/YSZ anode substrate was made at ORNL, the YSZ film was applied by colloidal spray deposition at NexTech, and the bi-layer element was co-sintered at 1400ºC.

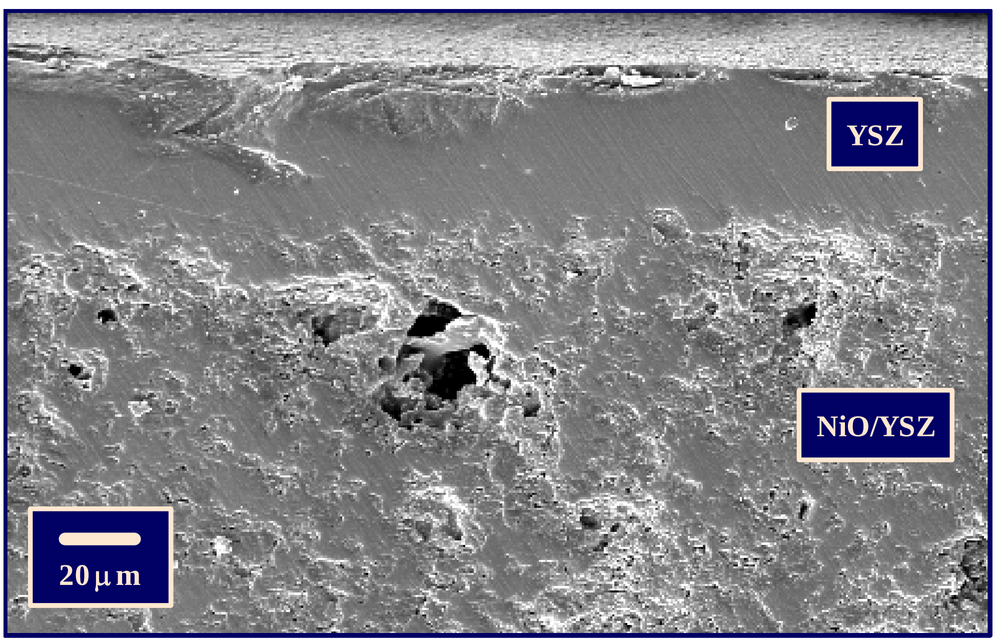

Figure 11. SEM micrograph of a polished cross-section of an anode-supported element prepared using processes developed at NexTech. Note the extremely high density of the YSZ electrolyte film. Also note that anode porosity is not evident in this micrograph due polymer intrusion into the pores during sample preparation.

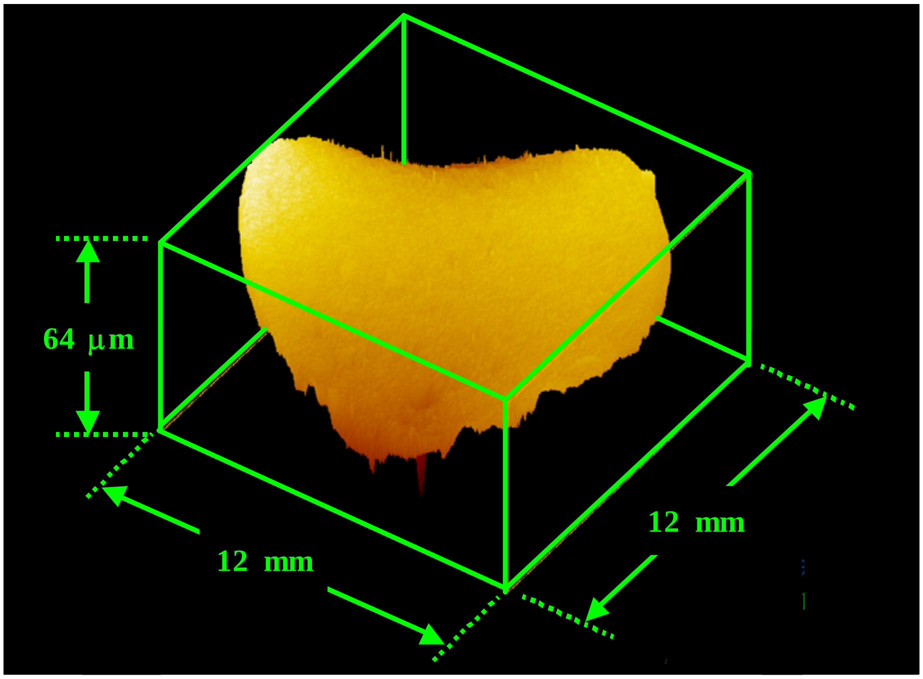

Figure 12a. Optical profilometry scan showing "Saddle-type" curvature observed in sintered LSM laminates, with non-optimized processing conditions.

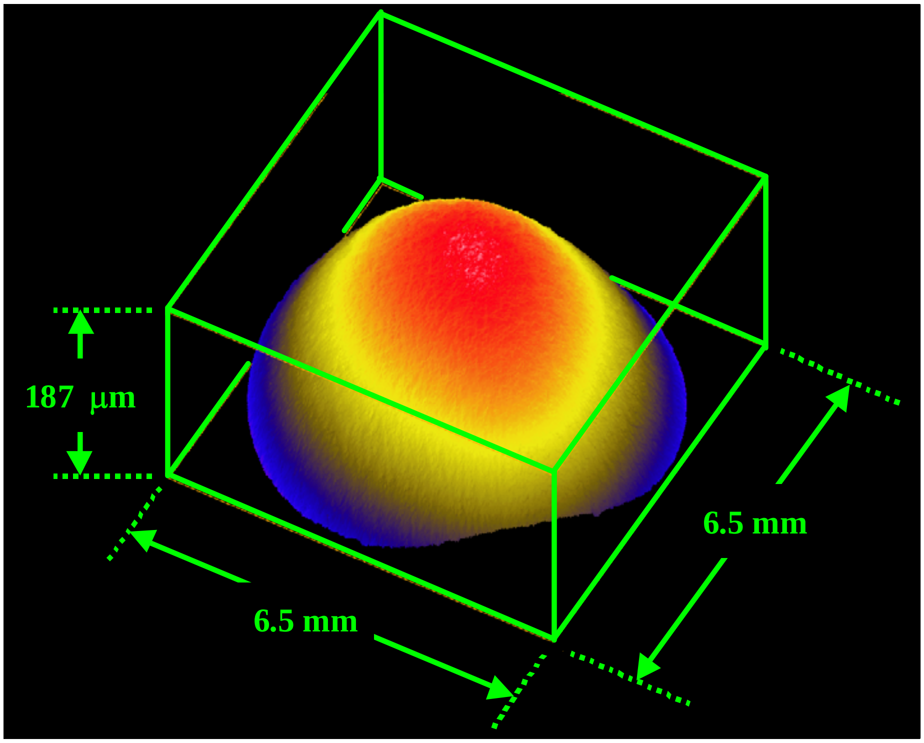

Figure 12b. Optical profilometry scan showing "one-way" curvature observed in sintered LSM laminates, with non-optimized processing conditions.

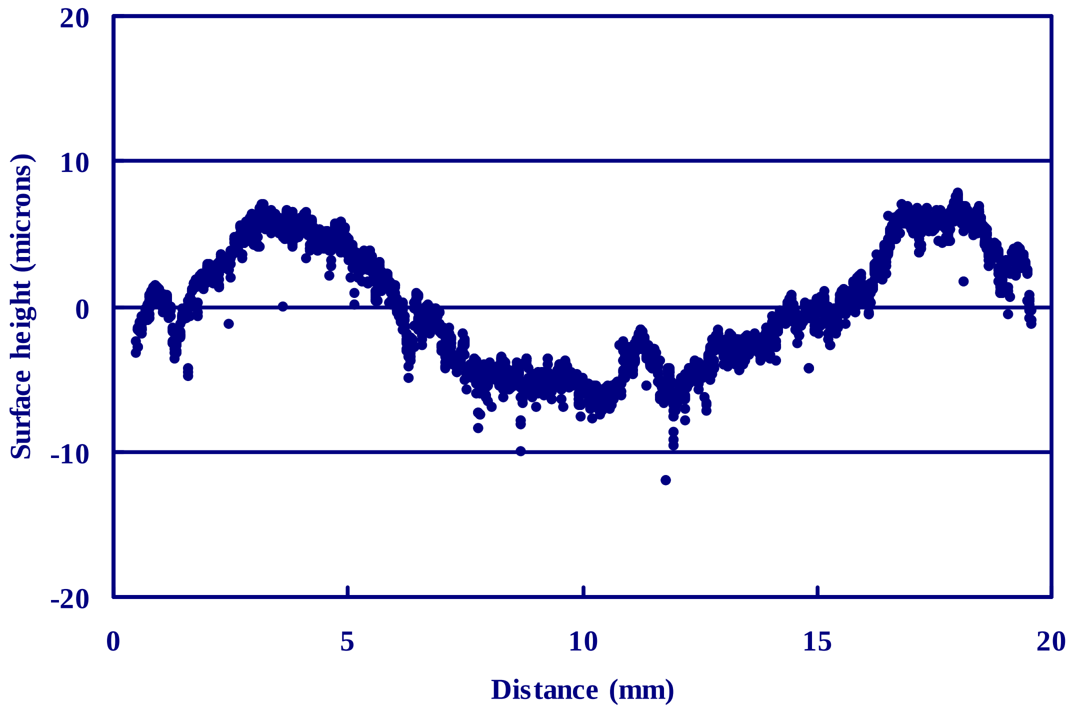

Figure 13. Optical profilometry scan of sintered LSM substrate prepared with optimized processing conditions (note total curvature of 15 microns over 2-cm length).

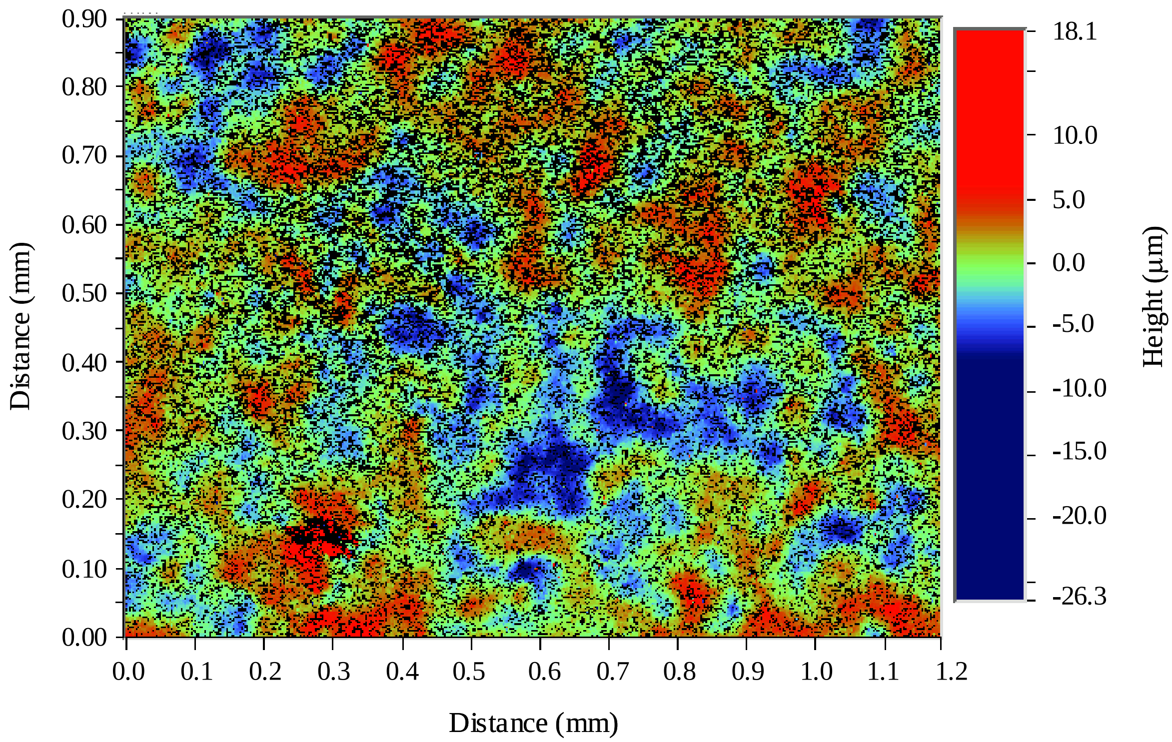

Figure 14. Optical profilometry scan showing surface topography over a 1-mm by 1-mm area of the interlayer coating shown in Figure 5.

Future Work (Phase III)

One of the key challenges that will be addressed in Phase III of this program is that there are multiple composition, processing and fabrication variables (see Figure 15) that need to be evaluated in order to optimize SOFC performance. Our Phase III test plan, which was delivered to DOE on October 25, 2001, was designed to meet this challenge, and the team is excited about the prospect of continuing this collaborative program and achieving a successful outcome.

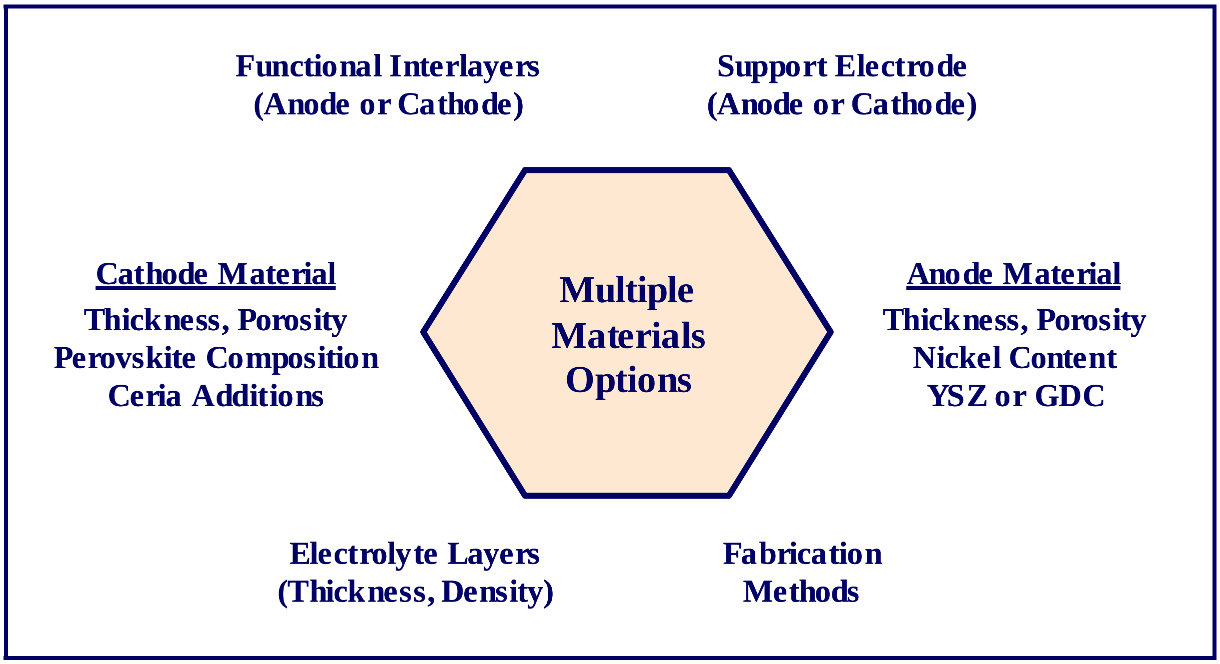

Figure 15. Multiple material options associated with optimization of SOFC performance.

APPENDICES