

Composite Ceria Electrolytes

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Over the past two years, NexTech Materials has been developing ceramic materials technology for applications in solid oxide fuel cells and other electrochemical systems. This work has been performed under a collaborative project funded by Ohio's Edison Materials Technology Center (EMTEC), and under three SBIR and STTR projects funded by the U.S. Department of Energy. The focus of NexTech's EMTEC project is the development of hydrothermal synthesis methods for producing nano-scale and crystalline powders of useful ceramic electrolytes. In a recently completed SBIR project, NexTech developed a new family of composite ceria-based ceramic electrolyte compositions providing a superior combination of electrical and mechanical properties. In a recent STTR project, NexTech collaborated with Lawrence Berkeley National Laboratory to apply colloidal deposition techniques to the fabrication of thin-film ceria fuel cells with excellent low-temperature SOFC performance. In an ongoing SBIR project, NexTech is collaborating with Westinghouse on the development of a low-cost process for depositing membrane films of yttria-stabilized zirconia onto lanthanum manganite air-electrode tubes. This paper describes the materials technologies being developed in these four projects.

NexTech's EMTEC Project

NexTech's EMTEC project was initiated in October of 1995 and runs through June of 1999. The objective of this project is to develop innovative ceramic powder synthesis and fabrication methods for the manufacture of oxygen-conducting ceramic membranes. Targeted applications include solid oxide fuel cells, oxygen generation systems, and ceramic membrane reactors. Team members are listed below:

- NexTech Materials
- University of Cincinnati
- Argonne National Laboratory
- Lawrence Berkeley National Laboratory
- Pacific Northwest National Laboratory
- Sandia National Laboratories
- Institute of Gas Technology
- Eltron Research
- Orton Ceramic Foundation
- Superconductive Components, Inc.
- DAI Ceramics
- Westinghouse
- BP Chemicals
- Litton Life Support
- SOFCo
- Babcock & Wilcox
- Motorola
- Coulter Corporation
- Consolidated Natural Gas
- Columbia Gas
- Plastronic, Inc.

NexTech is utilizing hydrothermal synthesis methods (see Figure 1) to produce zirconia and ceria-based ceramic electrolytes. NexTech’s hydrothermal process is based on a coprecipitation step (i.e., neutralization of aqueous acid solutions), followed by a mild hydrothermal treatment (i.e., at temperatures less than 300°C and pressures less than 15 MPa). The process results in the formation of an aqueous suspension of nano-scale (5-15 nm) crystallites with the cubic fluorite structure typical of zirconia and ceria-based electrolyte materials. A TEM micrograph of a hydrothermally produced powder of a $(\text{Ce}_{0.80}\text{Gd}_{0.20})\text{O}_{1.90}$ powder produced by this process is shown in Figure 2. As-produced zirconia and ceria-based electrolyte powders have large surface areas ($>100 \text{ m}^2/\text{gram}$), consistent with their nano-scale crystal size. An advantage of the hydrothermal process is the flexibility of product forms, such as dispersed aqueous suspensions, non-aqueous suspensions, or dried nano-scale powder. The surface area can be controlled over a wide range, either by modifying initial hydrothermal synthesis conditions, or by calcining dried powders at modest temperatures (see Table 1).

In this project, NexTech is conducting process development and materials characterization, evaluating sintering performance and electrical properties, and providing samples for evaluation by participating team members and other collaborators. NexTech has shown that hydrothermally derived zirconia and ceria-based powders can be sintered to high density at relatively low sintering temperatures. For example, an SEM micrograph of a 98% dense gadolinium-doped ceria ceramic, sintered at 1250°C, is shown in Figure 3.

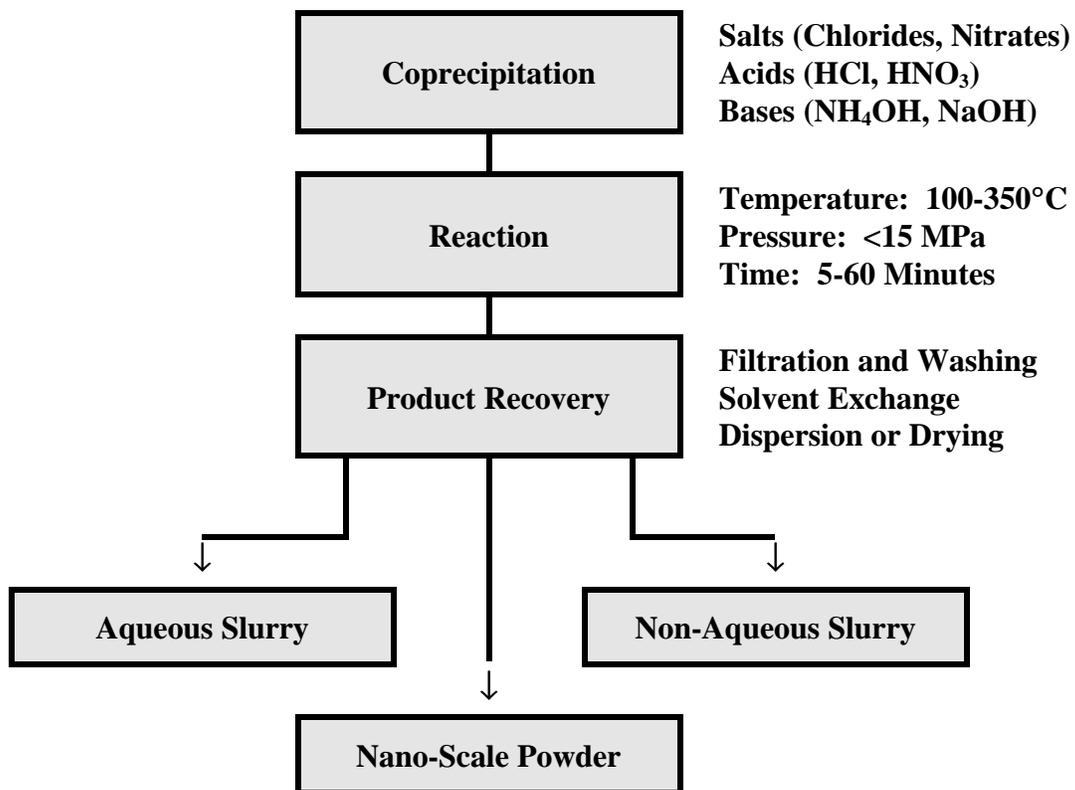


Figure 1. NexTech’s Hydrothermal Powder Synthesis Process.



Figure 2. TEM micrograph of a hydrothermally derived Gd-doped ceria powder.

| Table 1. Surface Area of Zirconia and Ceria Powders | | | |
|--|---|---|--|
| Calcination | BET Surface Area (m²/gram) | | |
| | (Zr_{0.852}Y_{0.148})O_{1.926} | (Ce_{0.80}Gd_{0.20})O_{1.90} | (Ce_{0.85}Sm_{0.15})O_{1.925} |
| as-produced | 154 | 126 | 127 |
| 600°C, 4 hours | 108 | --- | 79 |
| 700°C, 4 hours | 91 | 33 | 45 |
| 800°C, 4 hours | 65 | 18 | 25 |
| 900°C, 4 hours | 40 | 9.5 | 12 |
| 1000°C, 4 hours | 14 | 4.4 | 5.0 |

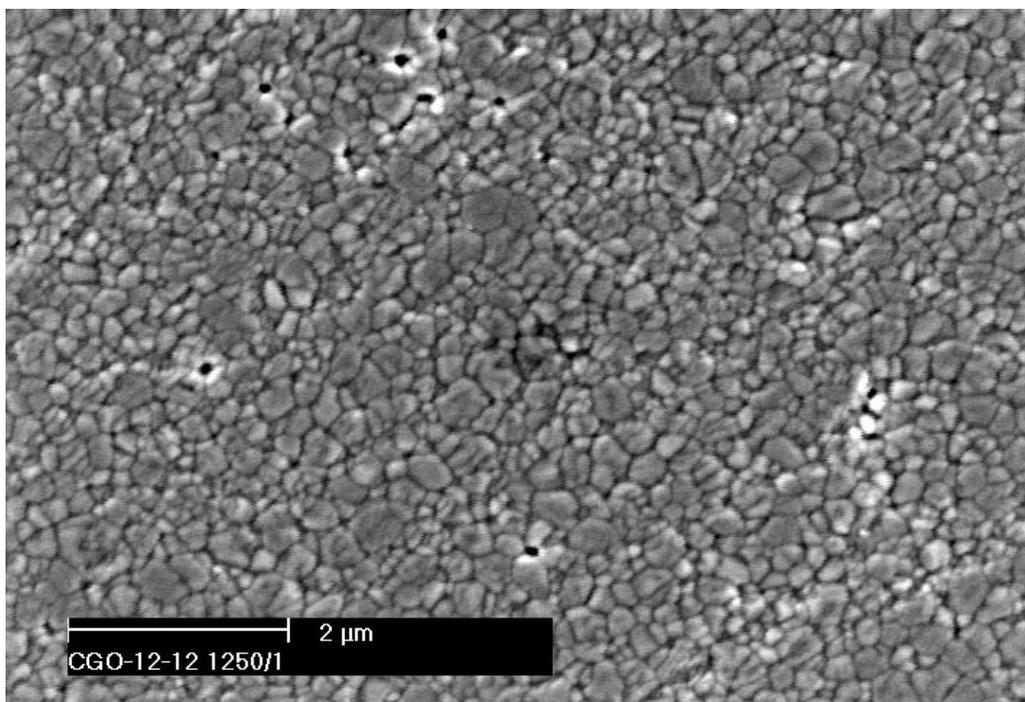


Figure 3. SEM micrograph of a hydrothermally derived Gd-doped ceria ceramic, sintered at 1250° C.

NexTech has completed a comprehensive set of two-lead electrical conductivity measurements on hydrothermally derived ceria-based ceramics. Two-lead measurements cannot differentiate between the contributions of electrolyte and electrode, and interfacial resistances. However, the two-lead method does allow for relative comparisons regarding effects of material composition, synthesis methods, and sintering conditions. For example, with platinum electrodes, a profound effect of sintering temperature on two-lead conductivity was observed (see Figure 4). The conductivity decreased as the sintering temperature was increased above 1300°C; this trend was common to all of the hydrothermal ceria ceramics evaluated. These results suggest either highly conductive grain boundaries in the fine-grained ceria ceramics sintered at low temperatures, and/or dopant segregation at grain boundaries in coarser-grained ceria ceramics sintered at higher temperatures. Additional microstructural characterization, in combination with ac impedance spectroscopy, may be needed to clarify specific causes.

The two-lead method also provides a means to compare the electrochemical performance of different electrode materials, as shown for Gd-doped ceria ceramics in Figure 5. Compared to platinum and silver electrodes, the conductivity was almost doubled by using cermet electrodes comprised of (La,Sr)(Co,Fe)O₃ and silver phases. Since identical ceramic samples were used, the improvement can only be related to superior electrochemical performance of the cermet LSCF/Ag electrodes. However, additional work is needed to determine whether composition or morphology of the electrode was responsible for the improvement.

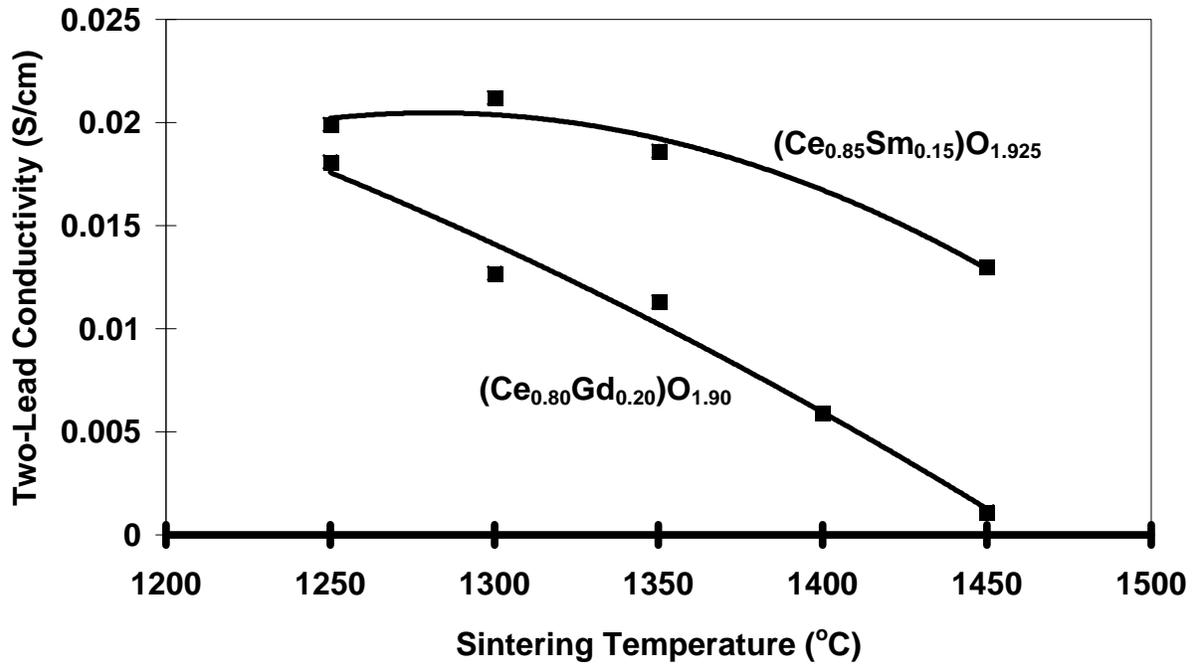


Figure 4. Two-lead conductivity versus sintering temperature for hydrothermally derived ceria-based ceramics (platinum electrodes).

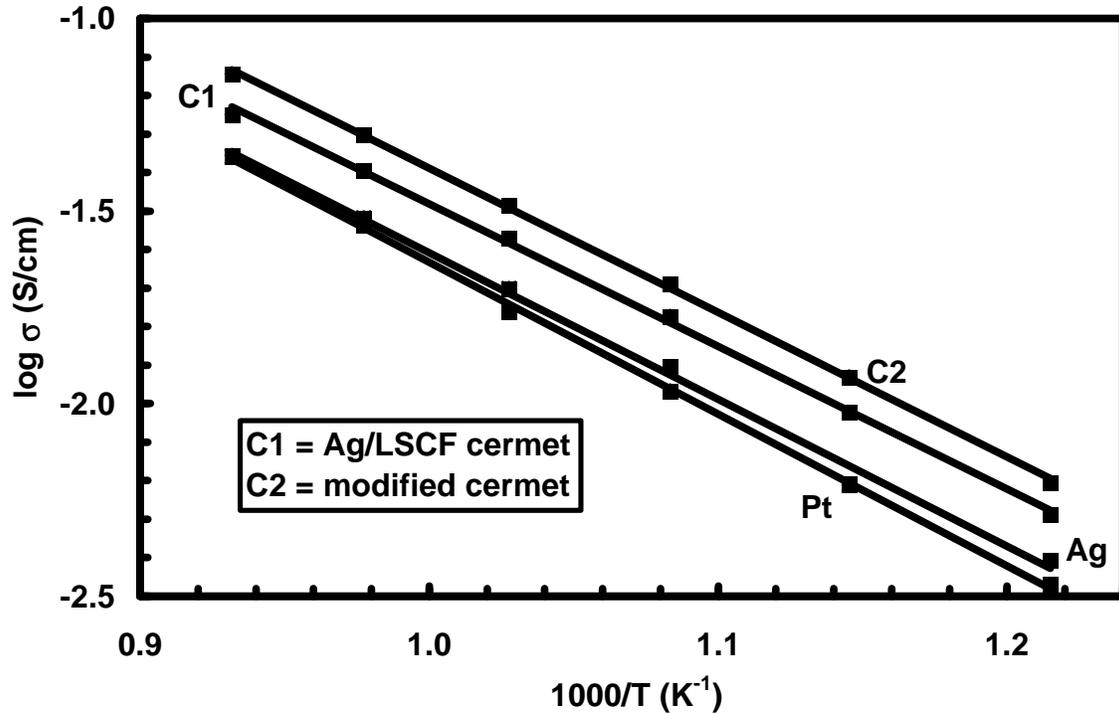


Figure 5. Arrhenius plots of two-lead conductivity versus reciprocal temperature for hydrothermal (Ce_{0.80}Gd_{0.20})O_{1.90} ceramics with different electrode materials.

Thin-Film Ceria Fuel Cells

In this STTR project, NexTech Materials and Lawrence Berkeley National Laboratory (LBNL) collaborated on the fabrication of thin-film ceria fuel cells and evaluation of their low-temperature SOFC performance. Contract information is provided below:

- **Title:** *Thin-Film Ceria Fuel Cells with Low Operating Temperature*
- **Sponsor:** U.S. Department of Energy, Office of Transportation Technologies
- **Contract Number:** DE-FG02-96ER86051
- **Period of Performance:** 6/22/96 - 3/21/97
- **Contracting Officer:** Dr. JoAnn Millikin (202-586-2480)
- **Subcontractor:** Lawrence Berkeley National Laboratory
- **Principal Investigator:** Dr. Scott L. Swartz (614-842-6606)

Several developers have shown that deposition of thin-film yttria-stabilized zirconia (YSZ) membranes on porous electrode (anode or cathode) supports is a feasible approach to reduce the operating temperature of solid oxide fuel cells. However, even with thin-film YSZ membranes, the SOFC operating temperatures cannot be reduced to below 600°C, without substantial degradation in performance and efficiency. The use of higher-conductivity electrolyte materials, fabricated in thin-film configurations, is the most feasible approach for reducing SOFC operating temperatures to below 600°C. It is well known that ceria-based ceramic electrolytes have higher conductivity than YSZ, especially at temperatures below 600°C. A common problem with ceria-based electrolytes has been the onset of electronic conductivity at high temperatures, which reduces efficiency of SOFC operation. However, at temperatures below about 600°C, electronic conductivity of ceria-based electrolytes is negligible, so that SOFC performance is not degraded. Thus, this STTR project was undertaken to evaluate ceria thin films as an approach for reducing SOFC operating temperatures to 600°C and below. Successful development of the technology demonstrated in this project will open up opportunities for SOFCs to compete as lower cost and higher performance options to PEM-based fuel cells for future transportation applications.

The approach pursued in this project was based on the synergistic combination of NexTech's hydrothermal synthesis process for preparing nano-scale ceria suspensions (as discussed above and shown in Figure 1) and LBNL's colloidal deposition method for fabricating thin-film fuel cells. The colloidal deposition process, as shown in Figure 6, is an inexpensive approach for fabricating bilayer electrolyte elements comprised of an electrolyte film on a porous electrode substrate. A colloidal suspension of the desired electrolyte material is first prepared, and then cast onto a highly porous electrode plate. A green electrolyte film is formed as the solvent evaporates from the suspension, and then the bilayer is sintered so that the electrolyte film densifies fully and the electrode substrate densifies partially. If the relative shrinkages and green densities of the two layers are properly controlled, then the process results in a bilayer element comprised of a dense electrolyte film (10-15 μm thick) on a porous and flat electrode substrate (200-300 μm thick). This process was successfully applied to the fabrication of a $(\text{Ce}_{0.80}\text{Gd}_{0.20})\text{O}_{1.90}$ (CGO) electrolyte film on a porous NiO/CGO anode substrate. An SEM micrograph of a cross-section of a sintered bilayer is presented in Figure 7, which clearly shows the pore-free nature of the CGO film.

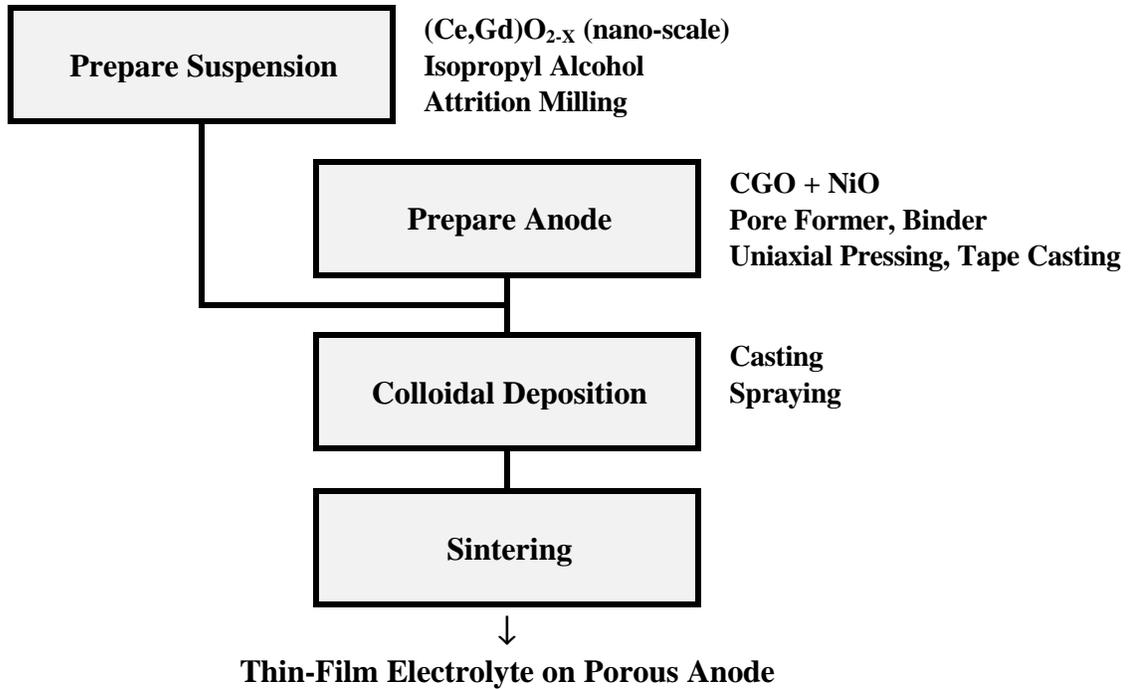


Figure 6. LBNL's colloidal deposition process for fabricating thin-film fuel cells.

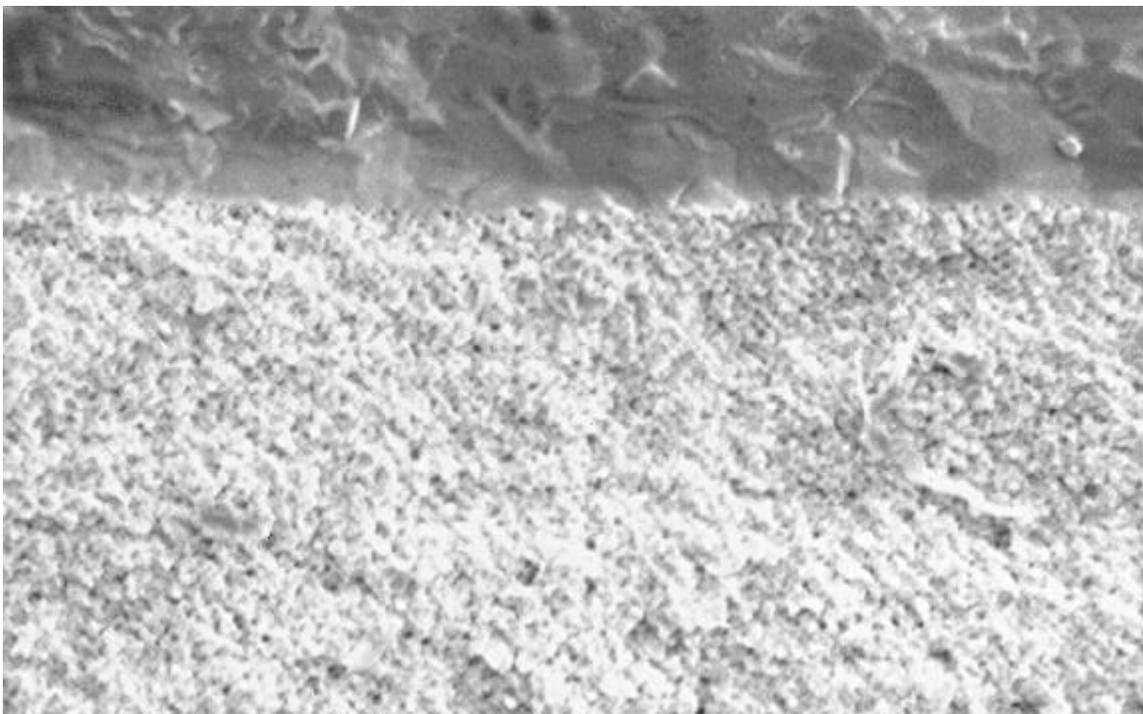


Figure 7. SEM micrograph of a cross-section of a bilayer element comprising a porous NiO/CGO anode with a dense CGO electrolyte film.

After successful fabrication of sintered bilayers, fuel cell elements were completed by the deposition of a (La,Sr)CoO₃-based cathode. Fuel cell testing was conducted using H₂ and air as fuel and oxidant, and the power density curves obtained are presented in Figure 8. To our knowledge, the power densities achieved (~650 mW/cm² at 750°C) in the thin-film ceria cell represent the *highest ever reported* for a ceria-based solid oxide fuel cell. The power density achieved at 600°C (~270 mW/cm²) also represents one of the highest values reported for *any type of fuel cell* operating at this temperature. These results are especially promising, given the limited amount of optimization work directed at the anode microstructure and the cathode material.

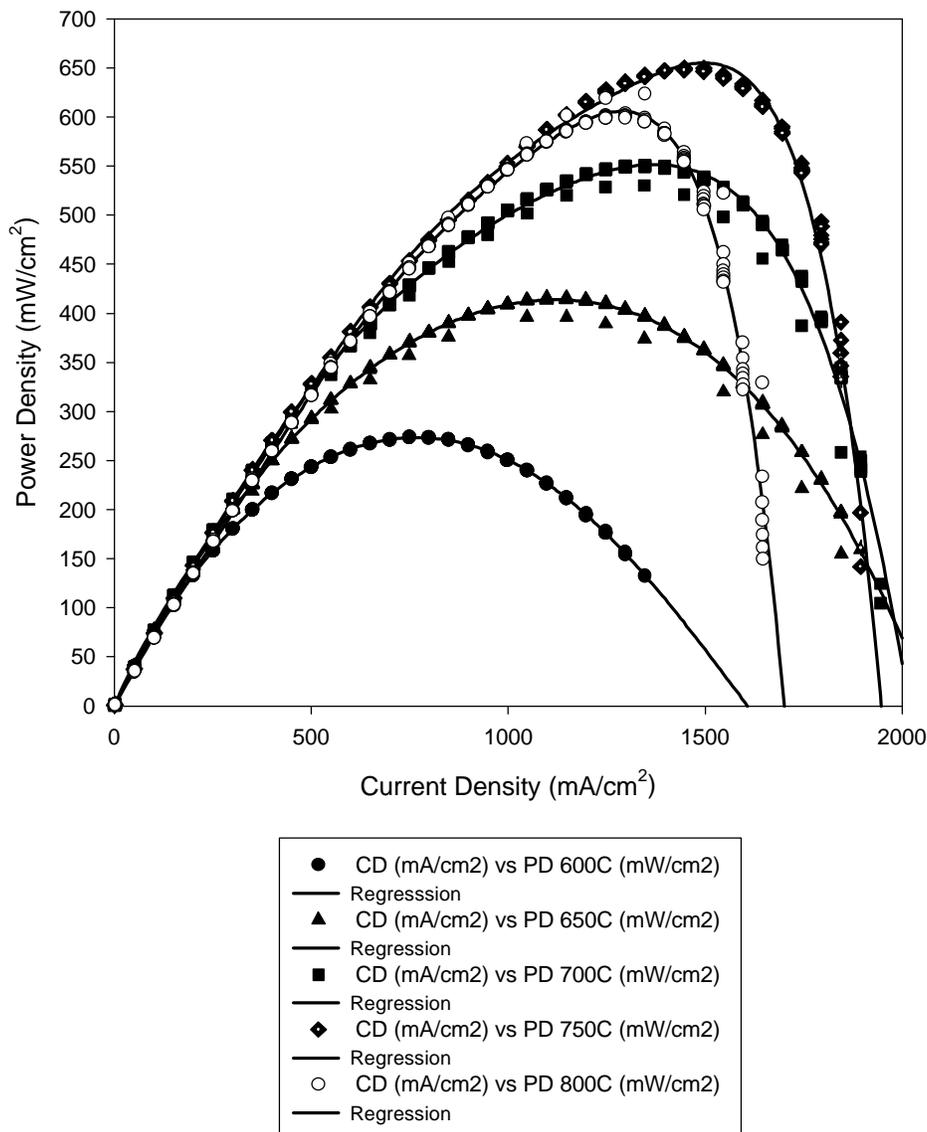


Figure 8. Power density versus current density curves at different temperatures for a colloiddally deposited thin-film ceria fuel cell.

Composite Ceria Electrolytes

In this recently completed SBIR project, NexTech Materials demonstrated a novel composite materials approach for improving the performance of ceria-based ceramic electrolytes. The objective of this project was to improve the oxygen ion transference number of ceria-based electrolytes, through the controlled addition of a nano-dispersed insulating second phase. Contract information is provided below:

- **Title:** *Composite Ceria Electrolytes for Solid Oxide Fuel Cells*
- **Sponsor:** U.S. Department of Energy, Federal Energy Technology Center
- **Contract Number:** DE-FG02-96ER82236
- **Period of Performance:** 8/13/96 - 3/6/97
- **Contracting Officer:** William Cary Smith (304-285-4260)
- **Principal Investigator:** Dr. Scott L. Swartz (614-842-6606)

Based on their relatively high oxygen ion conductivities, doped cerium oxide ceramic electrolytes are potential electrolyte materials for intermediate-temperature solid oxide fuel cell applications. However, the utilization of single-phase ceria electrolytes in SOFCs has been limited by electronic conductivity (which results in power loss) and by poor mechanical properties (which leads to failure of planar electrolyte elements). NexTech's approach to solving these problems involved the controlled addition of an insulating second phase to a nano-scale ceria powder, followed by the preparation of a composite ceria ceramic electrolyte. Previous theoretical and experimental work at Arizona State University suggested that the insulating second phase reduces electronic conductivity by trapping electronic charge carriers within space charge regions at the interface between the ceria and insulating grains. This program was conducted to evaluate this approach for improving the oxygen ion transport properties of ceria-based electrolytes.

NexTech's hydrothermal synthesis process was used to prepare nano-scale ceria-based powder, which when sintered, provided the desired two-phase microstructure, as shown in Figure 9. Sintered densities for all compositions were in excess of 95% theoretical, although densities exceeding 98% theoretical were obtained when the second phase content was less than 15 mol%, as shown in Figure 10. Two-lead conductivity measurements determined that the second phase addition reduced the conductivity, but this reduction was fairly small for second phase contents of less than 20 mol%, as shown in Figure 11. Galvanic cell measurements were inconclusive, but indicated an apparent improvement in oxygen ion transference number at $pO_2 \sim 10^{-22}$ atm. Additional measurements are needed to quantitatively determine the effect of the second phase on oxygen ion transport in these composite ceria ceramics. Perhaps, the most beneficial effect of the second phase addition was on the mechanical properties, as shown in Table 2. Compared to an unmodified ceria ceramic, the second phase addition (11 mol%) led to a significant improvement in hardness and a two-fold increase of fracture toughness, as shown below:

- **Fracture Toughness (K_{IC}):** $0.9 \rightarrow 1.8 \text{ MPa}\cdot\text{m}^{-0.5}$
- **Vickers Hardness (H_V):** $780 \rightarrow 940 \text{ kg/m}^2$

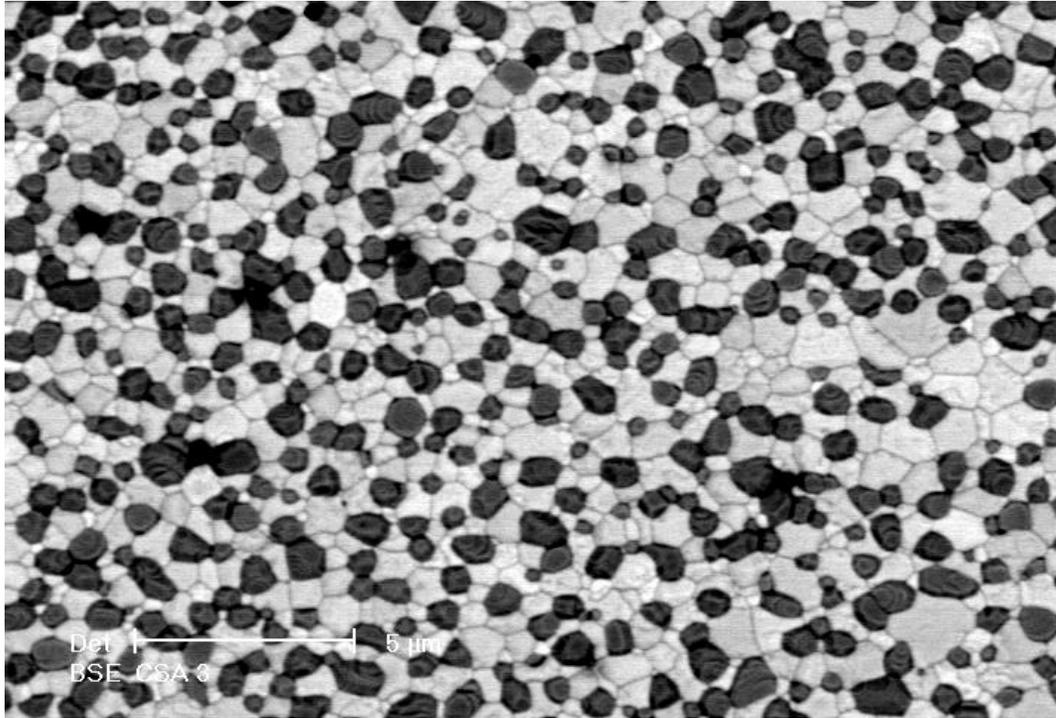


Figure 9. Backscatter-mode SEM micrograph of composite ceria ceramic.

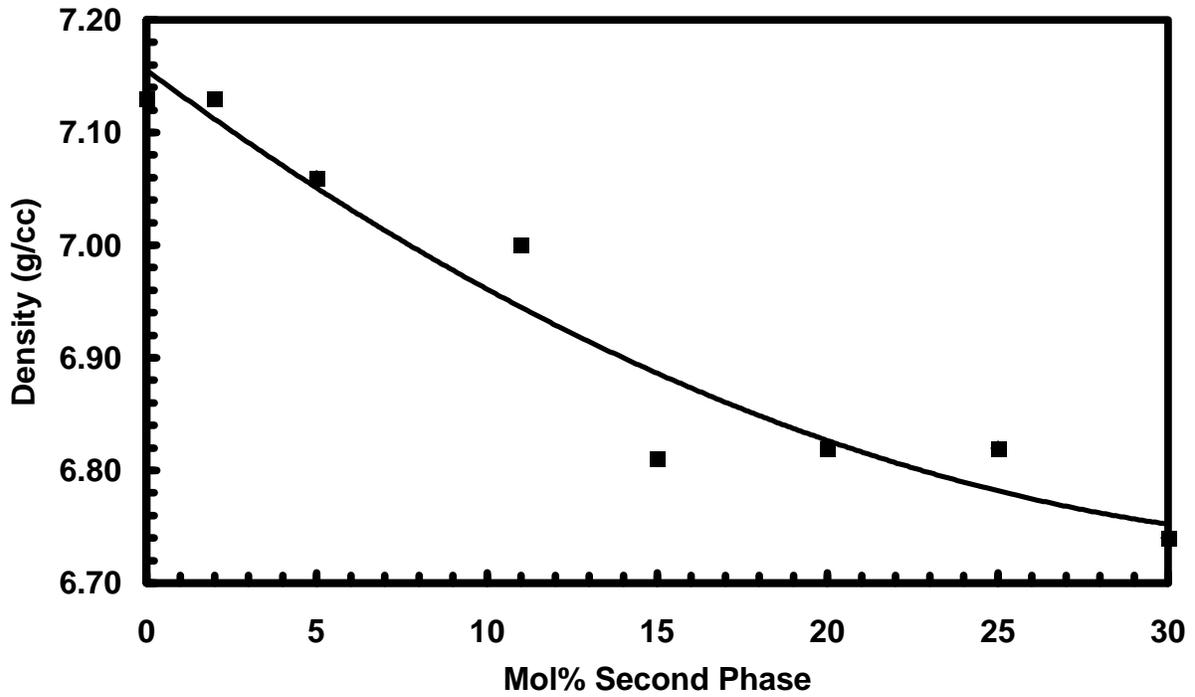


Figure 10. Effect of second phase content on the sintered density of composite ceria ceramic electrolytes.

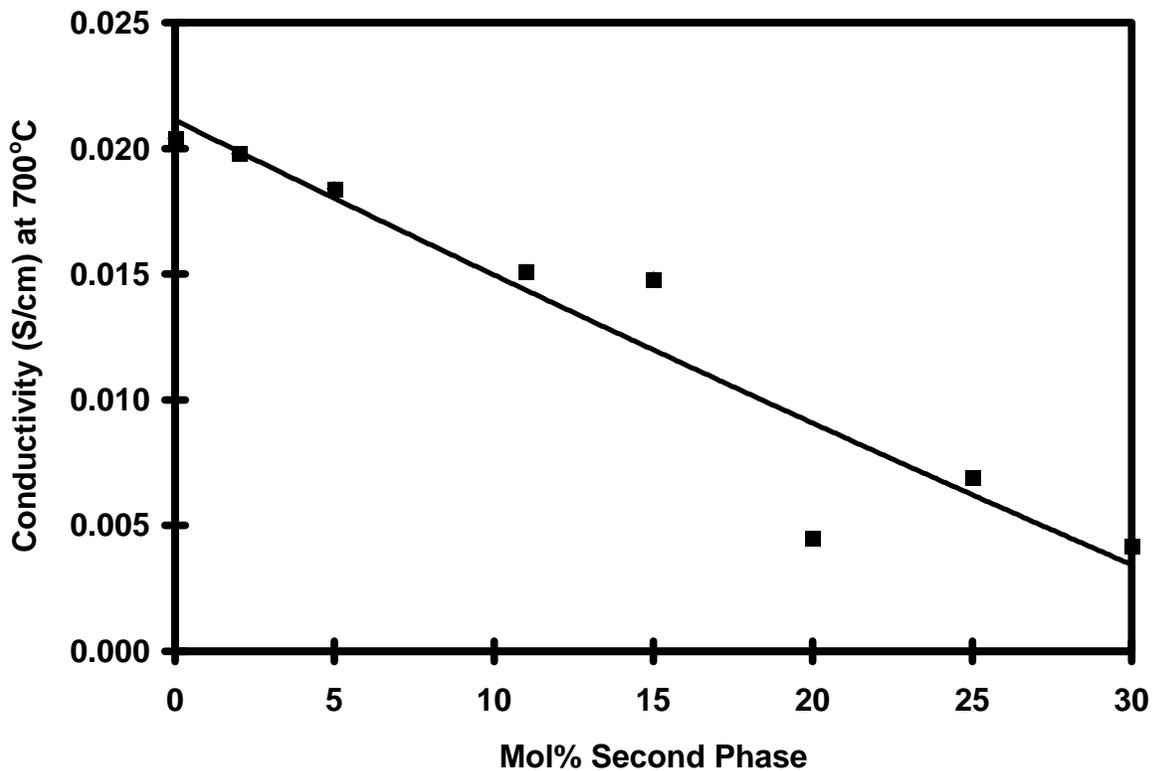


Figure 11. Effect of second phase content on the two-lead conductivity of composite ceria ceramic electrolytes (platinum electrodes).

Nano-Scale YSZ Electrolytes

NexTech Materials recently initiated an SBIR program, in collaboration with Westinghouse, to develop a low-coat electrolyte deposition process for the Westinghouse tubular SOFC, as a replacement for electrochemical vapor deposition. The approach is based on NexTech's hydrothermal synthesis process for making nano-scale YSZ powders. Electrolyte films will be deposited onto lanthanum strontium manganite (LSM) cathode tubes from colloidal YSZ suspensions, and then sintered to high density at low temperatures. With the low sintering temperatures possible with hydrothermal YSZ powders, adverse reactions between the YSZ electrolyte and the LSM cathode will be avoided. Contract information is provided below.

- **Title:** *Tubular SOFC with Deposited Nano-Scale YSZ Electrolyte*
- **Sponsor:** U.S. Department of Energy, Federal Energy Technology Center
- **Contract Number:** DE-FG02-97ER82443
- **Period of Performance:** 9/3/97 - 3/17/98
- **Contracting Officer:** William Cary Smith (304-285-4260)
- **Collaborating Partner:** Westinghouse
- **Principal Investigator:** Dr. Scott L. Swartz (614-842-6606)