VII.10 Advanced Thermal Spray Fabrication of Solid Oxide Fuel Cells

J. Brogan (Primary Contact), R. Gambino, R. Greenlaw, J. Gutleber
MesoScribe Technologies, Inc.
25 East Loop Road
Stony Brook, NY 11790
Phone: (631) 444-6455; Fax: (631) 444-6234; E-mail: jbrogan@mesoscribe.com

DOE Project Manager: Shawna Toth
Phone: (304) 285-1316; Fax: (304) 285-440; E-mail: Shawna.Toth@netl.doe.gov

Subcontractors: Boston University, Boston, MA; SUNY-Stony Brook, Stony Brook, NY

Objectives

- Optimize thermal spray parameters to produce dense deposits on cathode and anode supports.
- Minimize electrolyte thickness and ensure gas tightness.
- Maximize materials utilization.
- Determine microstructure and porosity evolution during spraying. Minimize porosity in electrolyte layer.
- Determine performance characteristics of solid oxide fuel cells (SOFCs) using electrolytes fabricated by High Definition Thermal Spray.

Approach

- Critically assess requirements for present and future SOFC systems and develop a realistic assessment of needs and capabilities.
- Identify and fabricate cathodic and anodic substrates for MesoScribe's deposition experiments.
- Deposit both yttria-stabilized zirconia (YSZ) and strontium-doped lanthanum gallate (LSGM) electrolytes on cathodic and anodic substrates using High Definition Thermal Spray.
- Characterize the cross-sections of deposited splats and electrolyte layers using optical and scanning electron microscopy (SEM).
- Measure the gas tightness of the as-sprayed deposited and post heat-treated electrolytes using a gas leak tester.
- Obtain the open circuit potential for cells characterized during this project phase and conduct impedance spectroscopy to reveal information about the cell ohmic resistance and interfacial polarizations.

Accomplishments

- High definition spray strategy was demonstrated for both YSZ and LSGM to meet DOE's goal of effective material utilization.
- High density, water-tight YSZ deposits were produced on both anodic and cathodic substrates in as-sprayed state. In general, YSZ layers in as-deposited state show intra-splat microcracks arising from relief of quenching stresses associated with solidification. This can be reduced or eliminated by a short heat treatment cycle. One goal is to lower this treatment temperature and to carefully design the anode/electrolyte/cathode manufacturing process to reduce steps.
- High density, water-tight LSGM deposits can be produced as-deposited, but they generally contain some degree of amorphicity. Again, this can be manipulated by controlling the degree of melting of the particles and/or through a low temperature sintering operation.

Future Directions

- Demonstrate advanced high definition thermal spray process as a means to deposit leak-tight YSZ and LSGM electrolyte on both anode- and cathode-supported cells in tubular, planar and Siemens Westinghouse HPD configurations.
- Identify the most appropriate means, compatible with thermal spray deposition of electrolyte, to engineer electrode-electrolyte interfaces with the goal of enabling the cell to undergo multiple thermal cycles (>100) and perform at high power densities (1 to 2 W/cm^2 on single cells).
- Demonstrate stoichiometric control of LSGM powders as a means to achieve single-phase perovskite phase in the as-sprayed state.
- Develop thermo-mechanical modeling methods to allow design of interfaces so as to aid in thermal mismatch management of the multilayer during either processing or service. Examine appropriate graded porosity concepts at the interface to achieve this requirement.
- Demonstrate high materials utilization (>70%) through high definition thermal spraying, particularly MesoPlasma process.
- Demonstrate atmospheric and MesoPlasma thermal spray processes as means to achieve high density, leak-tight YSZ electrolyte with minimal post spray heat treatment (<1200°C) through the application of advanced feedstock and processing strategies.

Introduction

Solid oxide fuel cell (SOFC) technology is expected to revolutionize power generation in the coming decades, given its higher energy efficiency, improved environmental performance and cost. The main impediment to SOFC implementation on a large scale is cell manufacturing cost. The challenge to lower the cost of SOFC manufacturing is being addressed through the development of advanced thermal spray methods for the fabrication of the electrolyte and, possibly, electrodes/interconnects. Thermal spray is a versatile, efficient, and cost effective approach to produce the ceramic fuel cell multilayers; however, conventional thermal spray may not be suited to meet the requirements of a modern fuel cell design. This is due to lack of effective microstructural control, interconnected porosity in electrolytes, and poor material utilization during deposition. MesoScribe Technologies Inc, in conjunction with program partners Center for Thermal Spray Research-SUNY-Stony Brook and Boston University, addressed these issues during the Phase I project. The research and development program addresses key DOE Small Business Innovation Research (SBIR) requirements in terms of effective material utilization, improved material characteristics and an integrated approach towards sequential fabrication of solid oxide fuel cells.

Approach

The basis of the effort lies in a breakthrough extension to modern day thermal spray technology through a *high definition* plasma spray capability and the ability to insert and deposit fine powders. This is coupled with use of advanced process map concepts to operate in parametric regimes that control specific microstructural features. Phase I effort concentrated on identifying key technical issues with respect to thermal spray fabrication of fuel cells. The processing effort concentrated on electrolyte deposition onto both anodic and cathodic substrates made by conventional powder processing routes. Both yttria-stabilized zirconia (YSZ) and strontium-doped lanthanum gallate (LSGM) have been deposited. Microstructural characterization was conducted in as-deposited and thermally treated materials. Water and gas leak tests were conducted to qualitatively assess the attributes of the sprayed layers to function as a high performance electrolyte. Finally, open circuit voltage and I-V measurements were made on the samples. The Phase I results demonstrate the potential of the technology and also identify key challenges and potential mitigating strategies. MesoScribe has communicated and discussed these developments with DOE National Energy Technology Laboratory (NETL) personnel as well as with our industrial partners. MesoScribe's goal is to develop and commercialize these advanced

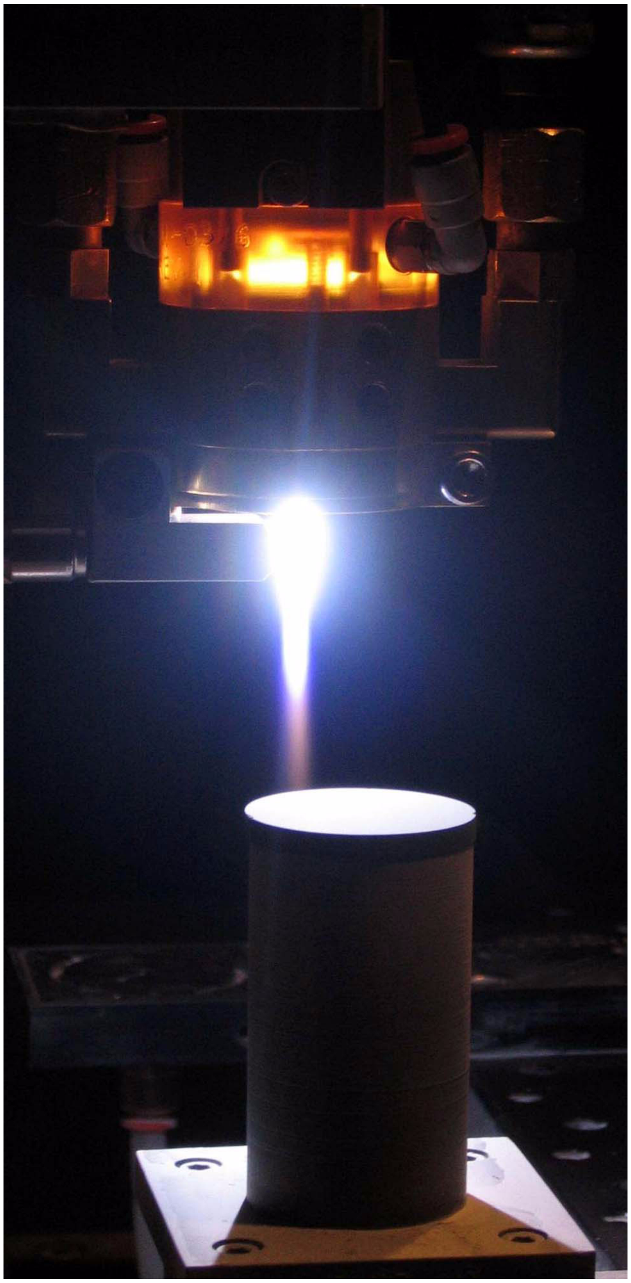

Figure 1. Demonstration of a High Definition Spray Deposition Process (Material: LSGM)

fabrication systems for implementation in fuel cell manufacturing. If successful, this approach has the potential to lower cell manufacturing cost while increasing throughput, both outcomes being key drivers in widespread fuel cell implementation.

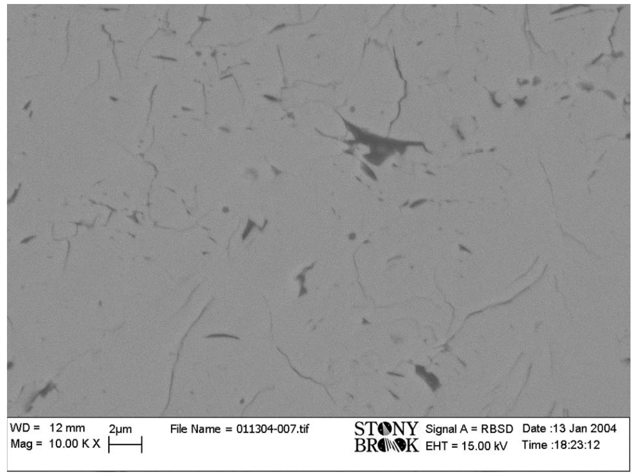

Figure 2. Cross-Sectional Micrograph of YSZ Showing Reduced Porosity in As-Deposited State

Results

MesoScribe, in conjunction with program partner Boston University, evaluated the important materials and processing requirements associated with thermal spray processing of SOFC electrolytes. System level considerations were also taken into account with respect to cathode, anode and interconnect materials. MesoScribe has successfully demonstrated that high definition spray deposition of both YSZ and LSGM can be achieved using the new technologies. Figure 1 illustrates the spray-plume substrate interaction on a disk that is approximately 1 inch (25 mm) in diameter. The plume size is in the range of 4-6 mm and can be scaled upwards. The research clearly shows that high target efficiency deposits can be achieved in planar or tubular cells with dimensions of 15 mm or more. For larger systems, the process can be appropriately rastered or scaled depending on the optimum processing ability.

A series of splat studies were conducted to evaluate the underlying characteristics of fragmentation and microcracking based on materials and processes. It was observed that LSGM splats did not undergo microcracking. Additionally, we were successful in obtaining fragmentation-free splats. Finer particle size and increased Reynold's number through MesoPlasma approaches yielded thinner

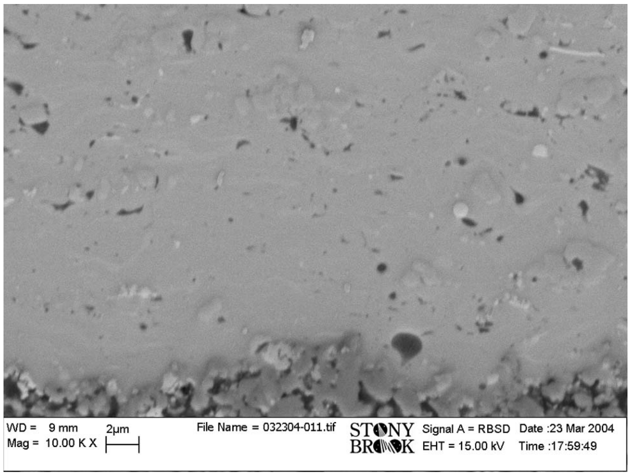

Figure 3. Mesoplasma-Deposited LSGM on Nio-GDC Anode. No Interfacial Layer Was Applied At This Stage (The as-deposited sample was water-tight)

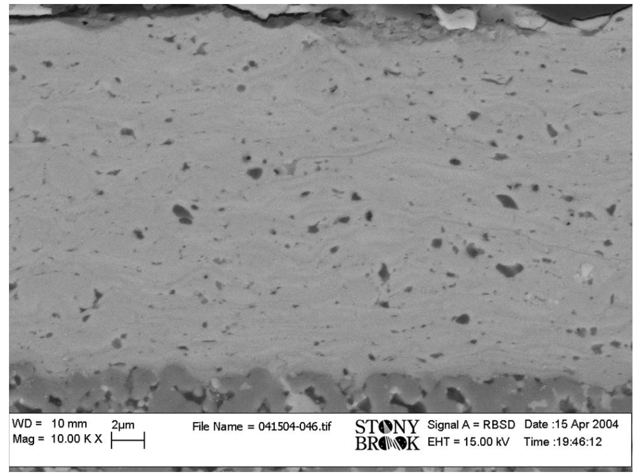

Figure 4. Mesoplasma-Sprayed LSGM on Nio-GDC after Low Temperature Heat Treatment for 30 Minutes (The sample shows increasing density but underwent macrocracking.)

splats, although quantitative studies need to be completed to assess reduction in splat thickness. Significant improvements in deposit density were achieved in the case of YSZ using the strategies outlined above (Figure 2).

Considerable effort in feedstock and parameter development enabled the fabrication of dense, water-tight LSGM electrolytes on Ni-GDC anodes. The deposit thickness was about 30 microns. A cross-sectional micrograph of the LSGM deposit in the as-sprayed state is shown in Figure 3, and a micrograph of the heat-treated LSGM is shown in Figure 4. Note the excellent interface between the LSGM layer and the anode. At this stage, we have not incorporated the interfacial barrier layer, but it is planned for Phase II.

As-sprayed and annealed LSGM layers were also characterized using x-ray diffraction (XRD) analysis. XRD traces obtained from as-sprayed LSGM layers can be indexed to a predominant perovskite phase with a broad low-angle, low-intensity peak which could not be identified conclusively. It is likely that this broad low-angle peak is indicative of an amorphous second phase. Upon annealing at 800°C for 30 minutes, two other phases were identified in the XRD trace of the annealed sample in addition to the original LSGM phase. They were indexed to a binary oxide with the stoichiometry $La_4Ga_2O_9$ and Ga_2O_3. A future goal is to obtain stoichiometric LSGM in the as-sprayed state.

Selected bi-layers of anode-YSZ electrolyte structures were post-spray annealed at 1300-1350°C. A two-layer cathode consisting of a lanthanum strontium manganese (LSM)-YSZ inner layer and a LSM outer layer was applied to the electrolyte through painting and firing at 1100°C for 2 hours. Prior to firing, platinum mesh current collectors were attached to the anode and cathode sides of the specimens. The completed cell was placed in a dual atmosphere test setup. Voltage-current density characteristics were obtained with flowing air on the cathode side and hydrogen humidified by bubbling through water at room temperature (composition of ~ 97% H_2/3% H_2O) on the anode side. The open-circuit potential was a little lower than the theoretically predicted value of 1.085 V but did not vary with flow rate once the flow rates of both air and humidified hydrogen were above 30 cc/min. This is indicative of a finite leak through the electrolyte which can be compensated by adding extra fuel. In the Phase I program, we have not performed detailed evaluation of the effects of leaks through ‘unhealed’ microcracks in the electrolyte. However, one of the tasks in Phase II will be to obtain more precise estimates of the effect of leaks through remaining microcracks on cell performance. The voltage-current density and power density-current density characteristics were obtained at 850°C. The maximum power density obtained was only ~45 mW/cm^2. Far higher power densities are expected once the electrode microstructure and porosity are carefully engineered, particularly near the interfaces.

Conclusions

The Phase I results demonstrate the potential capability of MesoScribe's advanced thermal spray process. The high definition plasma spray process was demonstrated to fabricate both YSZ and LSGM electrolytes onto both cathodic and anodic supported cells to meet DOE's goal of effective material utilization. High density, water-tight YSZ deposits were produced on both anodic and cathodic substrates in as-sprayed state. In general, YSZ layers in as-deposited state show intra-splat microcracks arising from relief of quenching stresses associated with solidification. This can be reduced or eliminated by a short heat treatment cycle. One goal is to lower this treatment temperature and to carefully design the anode/electrolyte/cathode manufacturing process to reduce steps. High density, water-tight LSGM deposits can be produced as-deposited, but they generally contain some degree of amorphicity. Again, this can be manipulated by controlling the degree of melting of the particles and/or through a low temperature sintering operation.

MesoScribe has effectively engaged both DOE NETL personnel and end use industrial partners for a successful transition of its efforts. MesoScribe's goal is to develop and commercialize advanced concepts and fabrication systems for implementation in fuel cell manufacturing. Together with DOE support and guidance from our industrial partners, a *concerted*, *integrated* effort is being made to innovate and enhance thermal spray technology for fuel cell manufacturing.