LOW-COST FABRICATION PROCESS FOR YSZ ELECTROLYTE FILMS

S.L. Swartz, M.M. Seabaugh, and W.J. Dawson
NexTech Materials, Ltd.
720-1 Lakeview Plaza Boulevard
Worthington, OH 43085

ABSTRACT

NexTech Materials is collaborating with Siemens Westinghouse on the development of a low-cost electrolyte deposition process to replace electrochemical vapor deposition for the Siemens Westinghouse tubular SOFC. The approach being pursued involves preparation of a dispersed suspension of nanoscale yttrium-stabilized zirconia (YSZ) crystallites, deposition of green YSZ electrolyte films onto lanthanum manganite (LSM) cathode tubes, and sintering of the deposited YSZ films to full density. A hydrothermal synthesis process is being used to prepare the nanoscale YSZ suspensions, and process enhancements have been made to achieve nearly complete dispersion of the YSZ crystallites in aqueous suspensions. Simple dip coating and spray coating methods are being used to deposit YSZ electrolyte films from the dispersed suspensions onto LSM tube sections. With suitable modifications to the suspension chemistry and deposition methods, sintered YSZ films have been prepared that are continuous and crack-free. Efforts also are underway to scale up the YSZ synthesis process using a novel continuous reactor system. NexTech’s recent progress on this program is described in this paper.

INTRODUCTION

The manufacturing process for the tubular SOFC elements for the Siemens Westinghouse solid oxide fuel cell (see Figure 1) involves the following sequential steps:

(a) fabrication of a porous (La,Sr)MnO$_3$ (LSM) cathode tube by extrusion and sintering;
(b) deposition of the (La,Sr)CrO$_3$ interconnect by plasma spraying;
(c) electrochemical vapor deposition (EVD) of a YSZ electrolyte film onto the LSM tube; and
(d) deposition of the Ni-YSZ anode by slurry coating and sintering. YSZ electrolyte deposition by EVD is the most capital-intensive step in this process. It is important that any YSZ deposition process under development be a direct replacement to EVD, so that modifications to the other fabrication methods are not needed. This defines the process requirements:

• The YSZ electrolyte film must be dense and crack-free and have sufficient thickness (>20 μm), to prevent non-electrolytic gas-flow paths between the anode and cathode.
• The deposition of the YSZ electrolyte film must not affect the porosity and/or morphology of the underlying LSM cathode tube.
• The maximum temperature during electrolyte deposition process must not exceed about 1300°C, to prevent any adverse chemical reactions between YSZ and LSM.

• The deposited YSZ film must be compatible with subsequent anode sintering.

![Tubular Solid Oxide Fuel Cell](image)

**Figure 1.** Schematic of Siemens-Westinghouse tubular SOFC design (1).

Colloidal deposition processes have been successfully demonstrated for the low-cost fabrication of planar solid oxide fuel cells with high power densities (2-3). These methods typically involve deposition of green YSZ films from non-aqueous suspensions onto non-sintered anode (nickel-YSZ) substrates, followed by co-sintering. The ability of the anode substrate to shrink during the co-sintering step alleviates constrained sintering effects that normally would occur with a pre-sintered substrate.

The colloidal processing method under development at NexTech involves film deposition from an aqueous suspension of nanoscale YSZ particles by dip coating or spray coating, followed by sintering of the film to promote densification and adhesion to the substrate. The key to success of this process is achieving high green density of the deposited YSZ films, so that sintering shrinkage, which leads to crack formation, is reduced. NexTech’s approach to developing a low-cost deposition method for YSZ electrolyte films, as a potential replacement to EVD, combines the following aspects:

1. use of a hydrothermal synthesis method for producing nanoscale YSZ powders that can be sintered to high densities at low temperatures (1200 to 1250°C), so that adverse chemical reactions between YSZ and LSM will not occur;

2. application of sound colloidal chemistry principles to develop dispersed suspensions of nanoscale YSZ crystallites with high solids loading and long-term stability;

3. development of low-cost dip-coating or spray-coating methods for depositing uniform and high green density YSZ electrolyte films on porous LSM tubes; and
development of sintering cycles designed to achieve densification of leak-tight YSZ films without cracking.

HYDROTHERMAL PROCESS DEVELOPMENT

Over the past several years, NexTech Materials has developed hydrothermal synthesis processes for producing zirconia and ceria based ceramic electrolyte compositions. This work has involved process development tailored to specific electrolyte compositions, process refinement to achieve dispersion of the nanoscale crystallites in aqueous and non-aqueous solvent systems, and scale up of the synthesis process.

Process Overview

The hydrothermal synthesis process (4), shown schematically in Figure 2, involves coprecipitation (i.e., neutralization of aqueous acid solutions), followed by hydrothermal reaction (i.e., at temperatures less than 300°C and pressures less than 15 MPa). During the hydrothermal reaction step, the constituent hydroxides are converted to crystalline oxide compounds. When applied to yttrium-stabilized zirconia, the process provides an aqueous suspension of nanoscale (5-10 nm) crystallites, typified by the TEM micrograph in Figure 3. A key attribute of the process is that crystallization occurs in the aqueous phase during hydrothermal treatment, so that high-temperature calcination treatments are not needed. Another advantage of the process is flexibility; the nanoscale materials can be produced as aqueous suspensions, non-aqueous suspensions, or dried nanoscale powder. Processing parameters can be tailored for control of characteristics such as surface area, particle size distribution, state of dispersion, and sinterability.

![Figure 2. Hydrothermal synthesis process for nanoscale oxide powders and suspensions.](image_url)
Continuous Production of Nanoscale Oxides

Scale-up of hydrothermal processes for production of nanoscale oxide powders and suspensions will be facilitated by the use of a continuous process, which will reduce capital costs associated with the high-pressure reaction step. In a collaboration with Pacific Northwest National Laboratory, NexTech Materials has designed and built a continuous reactor for pilot-scale production of its nanoscale materials. This tubular reactor, with a capacity of 1 kg/hour (dry powder basis), is shown in Figure 4. The reactor was designed to operate at relatively high temperature (up to 350°C) and pressure (up to 25 MPa). By operating at these extreme conditions, reactions can be completed within short residence times (30 to 60 seconds), thus reducing the overall size (and cost) of the full-scale production system. The reactor has been successfully operated for Pb(Zr,Ti)O₃, yttrium-stabilized zirconia (YSZ), and cerium oxide. As shown in Figure 5, identical x-ray diffraction patterns were obtained for nanoscale cerium oxide products from a four-liter autoclave (100-gram batch size) and from the continuous reactor.

DISPERSION OF NANOSCALE YSZ SUSPENSIONS

The successful utilization of nanoscale suspensions in coating processes will require ultimate dispersion of the nanoscale crystallites. Otherwise green densities of deposited YSZ films will be low, and excessive sintering shrinkage will cause cracks and delaminations. Dispersion of nanoscale oxides in aqueous solvents is complicated by the strong tendency of nanoscale crystallites to agglomerate and form much larger particles (due to van der Waals and other forces). If no effort is made to control agglomeration, the measured particle size distribution of hydrothermally prepared YSZ suspensions extends well into the micron range (compared to the YSZ crystallite size of 5 to 10 nm). Thus, a considerable amount of effort was applied to understanding the sources of agglomeration during the synthesis process and to identifying strategies to eliminate agglomeration.
Figure 4. NexTech’s continuous (1-kg/hr) hydrothermal reactor.

Figure 5. X-ray diffraction patterns of nanoscale cerium oxide produced in a small-scale batch reactor (bottom) and in NexTech’s continuous reactor (top).

Electrochemical Society Proceedings Volume 99-19
In order to improve dispersion (i.e., to reduce measured particle size), refinements were made to the entire synthesis process from preparation of the coprecipitated hydroxide feedstock suspensions, through hydrothermal reaction and processing of nanoscale YSZ product suspensions. A major portion of this work focused on increasing the charge on suspended particle surfaces as a means to improve dispersion. As shown in Figures 6 and 7, electrosteric surfactant additions were identified that increased surface charge of particles in the feedstock and product suspensions. These surfactants also extended the pH range of high particle surface charge so that dispersed suspensions can be prepared within moderate pH ranges. By applying these principles, high-quality dispersed YSZ suspensions were prepared in both acidic and basic pH regimes, as shown by their particle size distributions in Figure 8. Dispersion of the nanoscale YSZ crystallites was easier to achieve in the acidic pH regime – nanoscale YSZ suspensions were prepared with up to 35 wt% solids loading and a unimodal particle size of 6 nm, which is identical to crystallite size measured by XRD, TEM and surface area methods. However, dispersion of YSZ at low pH may result in significant leaching of yttrium from YSZ into the solvent, which could cause downstream problems related to non-uniform sintering. Currently, both dispersion routes are being pursued.

![Zeta potential versus pH curves obtained for yttrium-zirconium hydroxide feedstock suspensions, with and without electrosteric surfactant addition.](image).

**Figure 6.** Zeta potential versus pH curves obtained for yttrium-zirconium hydroxide feedstock suspensions, with and without electrosteric surfactant addition.
Figure 7. Zeta potential versus pH curves obtained for hydrothermally reacted YSZ product suspensions, with and without electrosteric surfactant additions.

Figure 8. Particle size distributions of dispersed YSZ suspensions.
Dispersed YSZ suspensions have been used for dip coating and spray coating onto two-inch long LSM tube sections. The primary technical challenge is the successful densification of the YSZ layer, which must overcome the constraints of the non-densifying substrate and avoid the formation of cracks due to lateral shrinkage stresses. This is being addressed by optimizing the particle size distribution of the dispersed YSZ suspensions. A particular advantage of this approach is that colloidal YSZ suspensions are produced directly by hydrothermal synthesis, and these suspensions can be dispersed (as discussed above) without an agglomeration-causing drying step. Initial process development work focused on deposition of YSZ electrolyte films from non-aqueous YSZ suspensions. This led to the successful demonstration of a continuous and crack-free (although not completely dense) sintered YSZ film shown by the SEM micrograph in Figure 8. Current work focuses on YSZ film deposition from aqueous YSZ suspensions. YSZ film deposition from aqueous suspensions will reduce cost (elimination of solvent exchange step and associated environmental management issues) and also will allow existing dispersion strategies to be employed. However, aqueous film deposition is complicated by the relatively high surface tension of water, which can lead to crack formation during drying. By controlling the particle size distribution and surface chemistry of the aqueous YSZ suspensions, crack-free and continuous sintered YSZ films were prepared from aqueous suspensions (see Figure 9). This film was prepared with a single deposition and sintering step (without repeated deposition and annealing cycles). Current work is aimed at increasing the green density of the deposited films, as a means to improve sintered density.

Figure 9. SEM micrograph of YSZ film deposited on an LSM Substrate from a non-aqueous suspension and sintered at 1250°C.
The hydrothermal synthesis process has been used to prepare aqueous suspensions of nanoscale yttrium-stabilized zirconia crystallites, and the synthesis process is being scaled up in a novel continuous hydrothermal reactor. Synthesis and processing methods have been refined to optimize the dispersion of these suspensions. The nanoscale YSZ suspensions are being used for development of a low-cost electrolyte deposition process as a potential replacement to electrochemical vapor deposition in the Siemens-Westinghouse tubular solid oxide fuel cell. YSZ films have been deposited onto porous LSM cathode tubes from both aqueous and non-aqueous suspensions, and these films have been successfully sintered to produce continuous, crack free YSZ films.

ACKNOWLEDGMENTS

Funding for this work is being provided by the U.S. Department of Energy and by Ohio’s Edison Materials Technology Center.

REFERENCES

1. The Westinghouse Solid Oxide Fuel Cell (FETC Project Facts, on the internet).
2. S. de Souza, et al., Solid State Ionics, 98, 57 (1997).
3. J.W. Kim, et al., Journal of the Electrochemical Society, 146, 69 (1999).
4. W.J. Dawson, Ceramic Bulletin, 67, 1673 (1988).

Figure 10. SEM micrograph of YSZ film deposited on an LSM Substrate from an aqueous suspension and sintered at 1250°C.