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SPECIAL SECTION/ADVANCED CERAMICS: Tailor Made

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Ceria materials tailored for pressing, casting and thick film deposition to fabricate electrochemical devices and catalyst supports.

Advances in doped ceria properties, processing and quality control are enabling the material's application in solid oxide fuel cells and electrochemical oxygen generators.

Doped cerium oxide materials, long valued and mass produced for catalysis, are now being applied to solid oxide fuel cells (SOFCs) and other electrochemical devices like electrochemical oxygen generators (ECOGs). For these new applications, developers are finding that the mass-produced materials are not meeting production or performance needs, or will not in the future as certain grades are retired. Focusing on the refinement of common ceramic processing methods and the development of subsequent quality control methods has led to a new series of reproducible doped ceria materials tailored to individual requirements.

Beneficial Properties

Cerium oxide powders, especially those doped with lanthanum or other metals, have well-known catalytic and oxygen conduction behaviors. These characteristics have revolutionized the catalytic converter and catalytic burner industries, particularly in transportation. The oxygen exchange capacity of ceria materials has fostered dramatic reductions in the amount of expensive precious metals, particularly platinum, needed to convert unspent fuels and toxic emissions into more benign gases.

More recently, ceria materials have begun to be applied to the challenges of fuel processing, particularly in the conversion of higher hydrocarbon fuels (i.e., gasoline) and fuels that contain sulfur compounds to simpler compounds that are more readily utilized. The oxygen exchange capacity and the attendant catalytic activity make doped cerias very attractive materials for use in SOFCs and ECOGs.

Ceria materials are being explored for electrodes, where catalytic oxygen conversion is very important, and for membranes/electrolytes, where high oxygen conductivity is of great value. A third application, in which ceria materials are used as barriers between manganite- or ferrite-based perovskite cathode materials and doped zirconia membranes, takes advantage of the low reactivity between cerias and perovskites.

However, doped ceria materials are not without their challenges. They are mechanically weak and are less than ideal for structural components, such as self-supporting membranes. Traditional ceria materials also require high sintering temperatures to achieve high density, which presents challenges for multi-layer fabrications where interactions of the layers with the environment or each other at high temperature can lead to reduced performance.

Processing Refinements

Scientists and engineers often come to materials suppliers requesting "standard" materials with the intention of adjusting the downstream processes to match the product they receive. Two reasons for this are the low cost of such materials and the unwillingness of some suppliers to alter their processes, since they produce materials that meet the demands of the sizable catalyst marketplace.

Unfortunately, it is always difficult-and often not possible-to adjust downstream processing to compensate for an inherent behavior of the standard material. Recently, scientists concentrating on the fine control of processing methods have yielded high-purity materials with reproducible morphology. The resulting materials are finely tailored to meet the processing and performance needs of individual applications and the larger industry.


Figure 1. ECOG device with thin-film, Gd-doped ceria membrane.

There are a number of routes for synthesizing doped ceria materials. Common synthesis methods include solid-state reactions and chemical precipitations, while exotic (and more expensive) methods include sol-gel and combustion synthesis routes. While both types of methods can produce high-performance materials at the R&D scale, quality (reproducibility) and cost are becoming more critical as ceria-containing electrochemical devices enter product demonstrations and the broader markets. Thus, focusing on refining the common, very controllable methods for producing high-performance materials at this market stage is yielding processes that can be cost-effectively scaled to larger production batches.

One method involves using chemical precipitation synthesis of amorphous precursor cerias. For nanoscale (<100 nanometer) cerias, the precursor is crystallized by hydrothermal methods. Such materials are used in catalyst production, as sintering aids and in composite (catalytic, interlayer) electrodes for electrochemical devices. Calcination and milling of the precursor is used to produce submicron-sized cerias over a wide range of Brunauer, Emmett and Teller (BET) surface areas, from 1 to 40 m^2/g. This range is required to tailor ceria for component and coating manufacture using methods such as tape casting, injection molding, extrusion, screen printing and spraying.

Such tailored cerias have been used to develop new membrane and electrode technologies for SOFC and ECOG devices in both electrolyte- and cathode-supported designs. An example of this, a cathode-supported tubular ECOG component, is shown in Figure 1. Gadolinum-doped cerias (GDC or CGO) are used to produce the thin (20 micron) gas separation/conduction membrane and the active (catalytic) cathodes fired onto an extruded doped lanthanum ferrite support tube.

Three layers, two active cathodes separated by a membrane layer, are sprayed onto the support and fired simultaneously. The active cathode is a patent-pending composite of the GDC and the doped lanthanum manganite material. The cerias are tailored to match the shrinkage of the cathode and have a sufficiently low sintering temperature to preserve an open pore structure in the cathodes during densification of the electrolyte into a defect-free membrane. A single ceria material would not sufficiently address both needs in this component, so multiple cerias are used.

In another example, a company is fabricating free-standing GDC membranes for pressurized systems, and therefore requires high mechanical strength. The company fabricates parts using tape casting, fires at temperatures below 1400°C, and can tolerate a somewhat higher surface area (up to 12 m^2/g). A series of composite materials was developed with additives designed to maximize strength while minimizing the effect on conductivity.

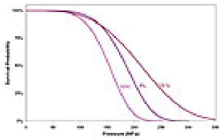


Figure 2. Weibull plot showing enhanced survivability of reinforced (5%, 10%) GDC over baseline GDC.

Figure 2 shows the Weibull plots of survivability vs. applied pressure. The survivability of the baseline GDC drops precipitously above 100 MPa, while reinforcement increases survivability to over 150 MPa. GDC containing 10% reinforcing material is the most forgiving, with nearly 60% survival probability at 200 MPa.

In a different instance, a powder that had a low surface area (< 10 m^2/g), yet fired to more than 96% dense at temperatures under 1400°C, was required. A key issue was that the processing of the powder into a green body yielded green densities below 50%. Since a common route for increasing fired density is to increase green density, this last requirement meant a tailored powder was required that achieved homogeneous packing in the green state, irrespective of component green density.

While the initial (baseline) material could sinter to >96% dense, it could not do so below the required 50% green density. Figure 3 shows that the baseline material required over 60% green density to attain 96% fired density. It was suspected that the broad particle size distribution of this material (which does work well in other applications) was hindering densification under these particular circumstances.

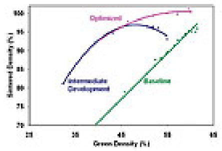
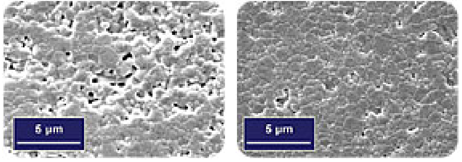


Figure 3. Sintered density vs. green density for optimized, intermediate and baseline ceria powders with <10m^2/g surface area.

Figure 4. Sintered structure of baseline material (a) vs. optimized material sintered from <50% green density (b).



Synthesis and milling conditions were optimized to yield powders with tighter particle size distribution. These powders led to significantly more uniform green compacts at lower green densities, which in turn yielded denser parts. The optimized material can attain the desired result from 45% green density, thus satisfying the need. The improvement in membrane structure is clearly demonstrated in Figure 4.

Quality Control is Key

In a similar situation, a company presented a series of very tight particle size distribution and surface area specifications for samarium-doped ceria (SDC or CeSmO). The current vendor had announced that it was going to stop producing the material, but the company needed very reproducible materials to help it enter the manufacturing engineering phase for its product. Three batches were produced that were chemically and physically similar, and exhibited essentially identical sintering behavior (see Figure 5).

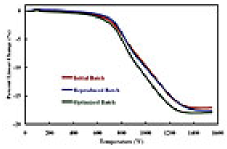


Figure 5. Dilatometry curves for three batches of SDC materials with nearly identical results.

Unfortunately, the materials did not process into tapes or sintered disks identically. While scanning electron microscopy (SEM) did reveal morphological differences, SEM is expensive and not a particularly quantifiable tool for gauging quality. In cooperation with the company, a simple, low-cost and quantifiable measurement was developed that correlated with the downstream processing. This method consists of fabricating a series of pellets using increasing pressures to achieve a range of green densities. The pellets are sintered in a single run, and their fired densities are measured. A typical plot is shown in Figure 6.

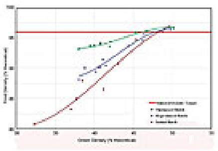


Figure 6. Sintered density vs. green density for SDC. Flatter curves correlate to better downstream processing.

The optimized batch (squares) shows the least variability of fired density with green density. It was subsequently determined that this material was the easiest to process into tapes and yielded the best product. This measurement method is now used as part of the quality assurance program for producing the powder for the client company.

A Refined Alternative

Commodity cerias cannot answer every application, particularly when tight processing, mechanical or electrochemical specifications are required. Several factors are necessary to provide the next generation of ceria materials that meet those needs: the ability to tailor powders for the required chemical and physical parameters, the use of low-cost powder fabrication processes that are readily scalable to larger batch sizes, and having the necessary quality controls in place to ensure reproducibility at every production scale. A flexible production model and continuous quality improvements will continue to meet the individual needs of each application now and as market demand grows.

For additional information, contact fuelcellmaterials.com, a division of NexTech Materials, Ltd., 404 Enterprise Dr., Lewis Center, OH 43035; (614) 842-6606; fax (614) 842-6607; e-mail sales@fuelcellmaterials.com; or visit www.fuelcellmaterials.com or www.nextechmaterials.com.

Figure 1 - ECOG Device with Thin-film Gd-doped Ceria Membrane

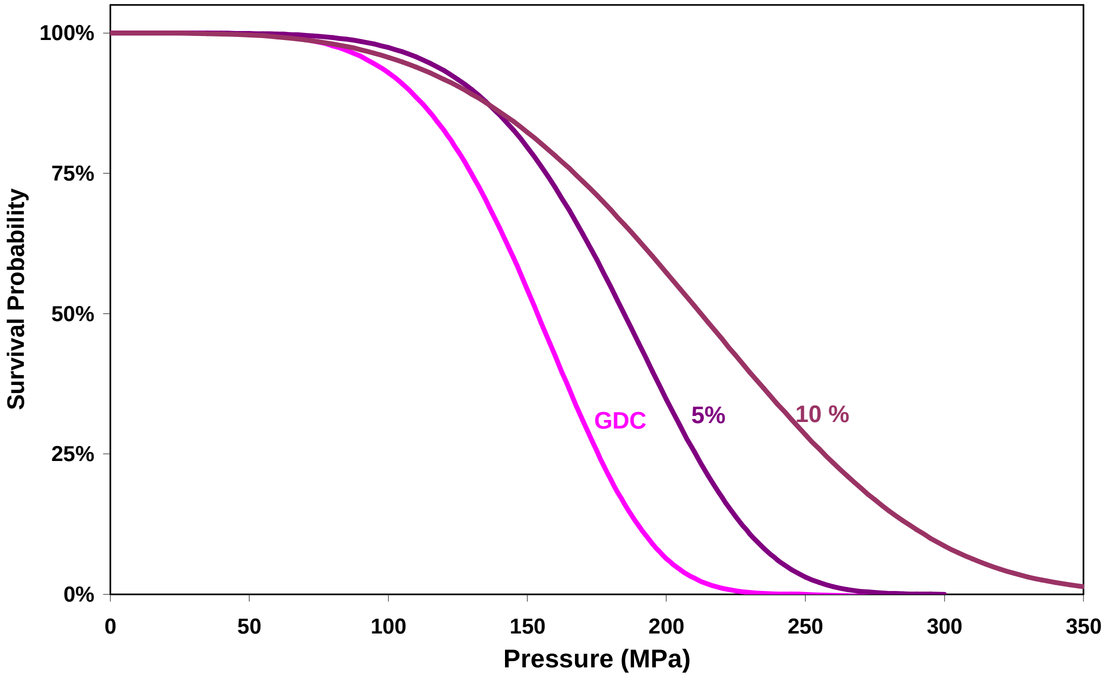


Figure 2 - Weibull Plot Showing Enhanced Survivability of Reinforced (5%, 10%) GDC over Baseline Materials (GDC)

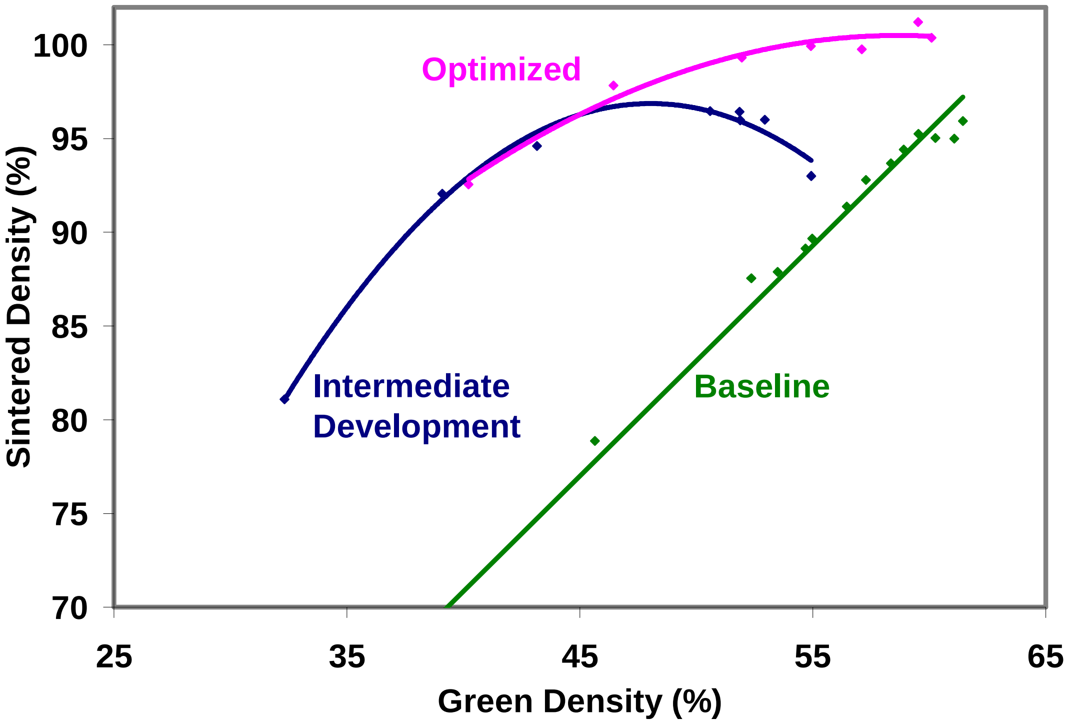


Figure 3 - Sintered Density Versus Green Density for Optimized, Intermediate and Baseline Ceria Powders with Surface Area <10 m^2/g

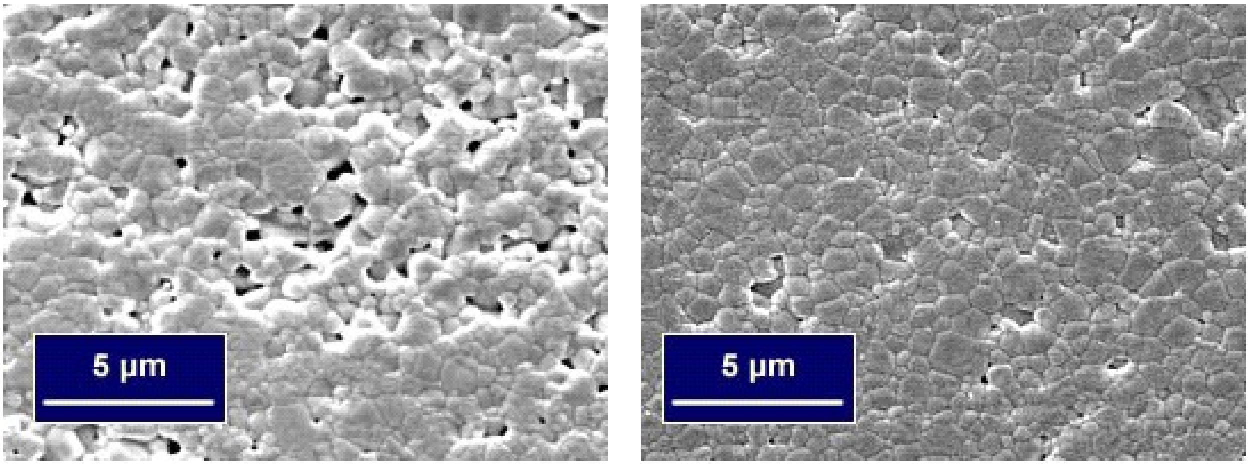


Figure 3a

Figure 3b

Figure 4 – 4a (left) Sintered Structure of Baseline Materials

4b (right) Structure of Optimized Material Sintered from Green Body that was <50% Dense

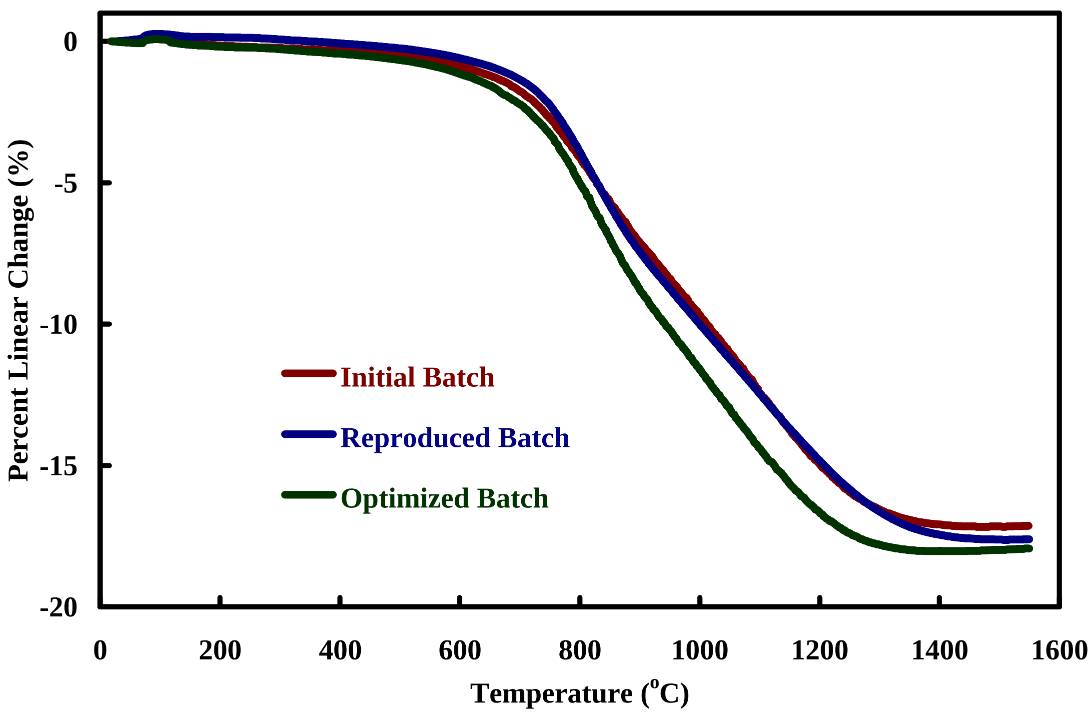


Figure 5 - Dilatometry Curves for Three Batches of SDC Materials

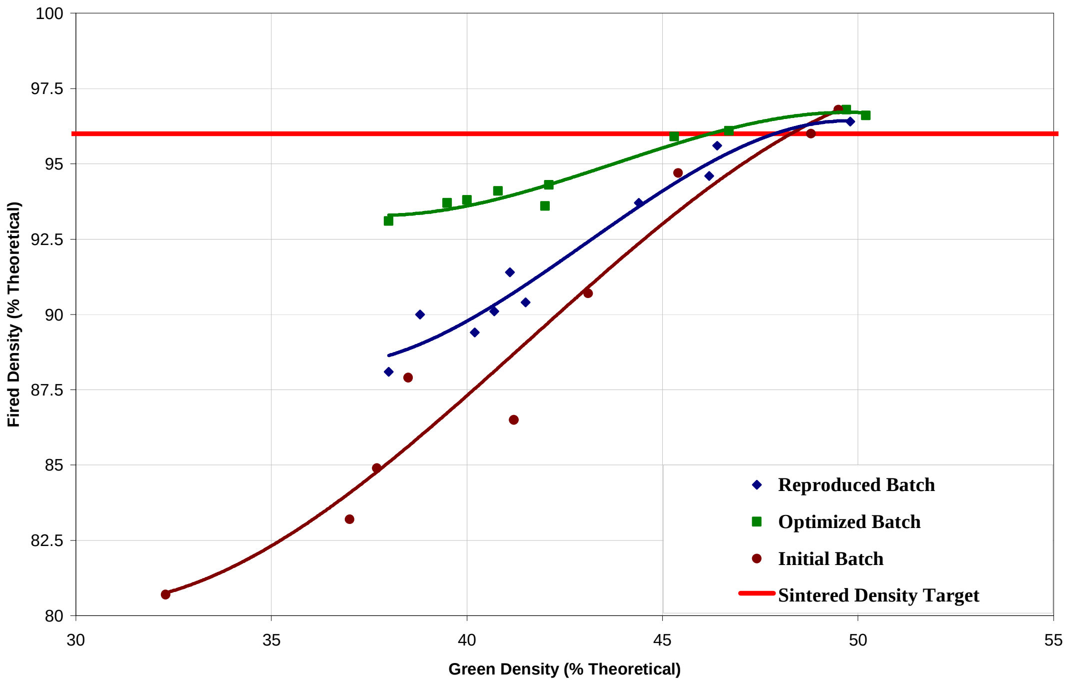


Figure 6 - Sintered Density Versus Green Density for SDC – Flatter Curves Correlate to Better Downstream Processing