APPLICATION OF LASER DIFFRACTION PARTICLE SIZE ANALYSIS TO SOLID OXIDE FUEL CELL MATERIALS

Solid oxide fuel cells (SOFC's) offer the potential to greatly reduce man's dependence on coal and oil for the production of electricity. They are clean, quiet and efficient. At the heart of these devices lies a complex combination of polycrystalline ceramic materials, each having to meet a particular set of structural and electrochemical requirements. Engineers control the performance of each component through manipulation of chemical and physical properties of the starting powders. Particle size is of critical importance to the powder properties and to the performance of the cells. Laser diffraction particle size analysis has proven to be an excellent way to monitor and control particle size for these materials during powder synthesis and component fabrication.

Introduction

An SOFC is a solid-state electrochemical cell that operates at temperatures between 600°C and 1000°C. The high temperatures needed for activation of conduction in the electrolyte require extensive use of ceramics for construction of the cell components. A typical SOFC is shown schematically in Figure 1. The electrolyte is a dense ceramic layer typically made from yttria-stabilized zirconia (YSZ) that acts as the medium through which oxygen ions are transported. The cathode is made of an electronically conducting ceramic material and has a porous microstructure. Newer cathode materials are mixed ionic/electronic conductors, which enhances their ability to ionize oxygen from the air to provide oxygen ions for conduction. The most common anode material is a NiO-YSZ composite. The anode has a porous microstructure to allow the flow of hydrogen to the anode/electrolyte interface. It must also be electronically conductive and withstand a severely reducing environment. Another ceramic material found in SOFC's is used for the electrical interconnections between the cells. This material must be electrically conductive and chemically stable in both

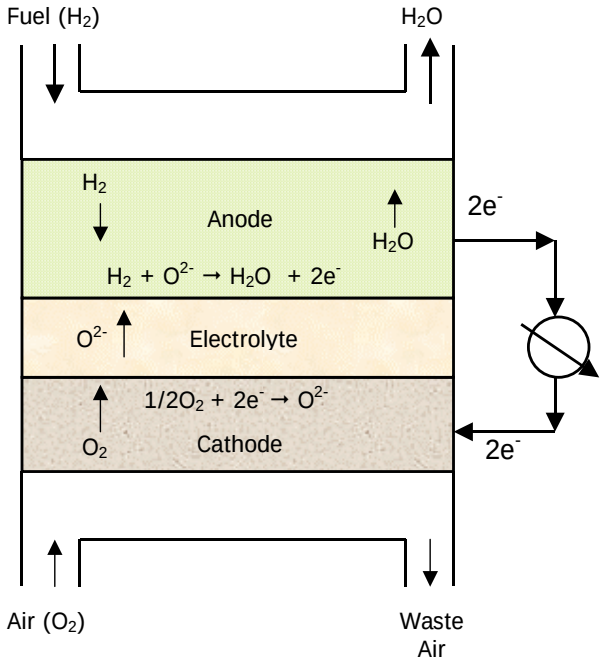

Figure 1

oxidizing and reducing atmospheres. All components need to have similar thermal expansion coefficients (TCE) over the wide temperature ranges of use in order to maintain the integrity of the structure. The devices typically require an electrolyte layer as thin as 10 µm or less. The electrodes can also be very thin and must have a controlled

pore structure that maximizes the interfacial area providing adequate gas flow and structural integrity. Meeting all these requirements with many different materials is a truly daunting task and poses a challenge for the fuel cell engineer.

Tools of the Trade

Fortunately, the engineer has some powerful tools to help meet this challenge. One tool is material chemistry. Selection of the proper material chemistry allows control of thermal expansion and interactions between different materials. Table 1 below lists some of the most common materials of construction for SOFC's. The cathodes are most commonly made from lanthanum manganate ceramics doped with strontium (LSM) to enhance conductivity and provide a TCE that closely matches that of the YSZ electrolyte. Recent designs have incorporated barrier layers of doped ceria between the cathode and electrolyte to inhibit reaction between the lanthanum and zirconia. Consequently, the thermal expansion of the electrode then needs to match the ceria layer. This is accomplished in part through the use of another ceramic, lanthanum strontium cobalt ferrite (LSCF). Yttria is added to NiO on the anode side to help match the TCE of the electrolyte.

Another tool engineers employ in fuel cell design is control of particle size distribution. Final porosity, transport properties and thermal expansivity can be tailored through control of starting particle size.

Table 1

Component	***Materials***
Anode	Ni-YSZ
Electrolyte	Y-ZrO_2
Cathode	$La_{(0.8)}Sr_{0.2}MnO_3$ $La_{0.6}Sr_{0.4}Co_{0.2}Mn_{0.8}O_3$
Interconnect	Doped $LaCrO_3$

Figure 2

An Example

This example describes the use of the Horiba LA-950 Partica laser diffraction particle size analyzer (Figure 2) for monitoring and control of the particle size distribution of a common cathode material during milling. The data is then used to demonstrate the use of particle packing calculations to determine the final porosity of a part made with this material.

The material under study is an LSCF compound synthesized via a solid-state process. Calcining the oxide mixture produces a somewhat coarse material that is subsequently milled to final particle size. Since the refractive indices for these materials are not readily available in the literature a suitable refractive index must be determined using another approach. The approach applied here was to utilize the LA-950 software, which allows the user to observe the effects of changes in optical model on the fit of the calculated intensity values to measured intensities. In this example, the values of Chi^2 and R were used to assess the appropriateness of the optical parameters employed in the analysis. The first step in this process was determining the real component as 2.0. Next a suitable imaginary component

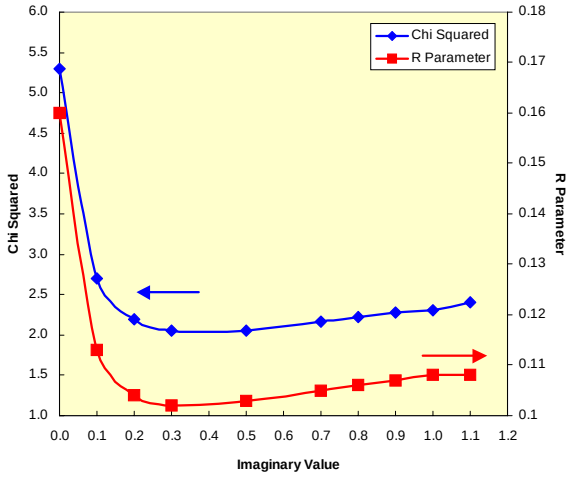

Figure 3

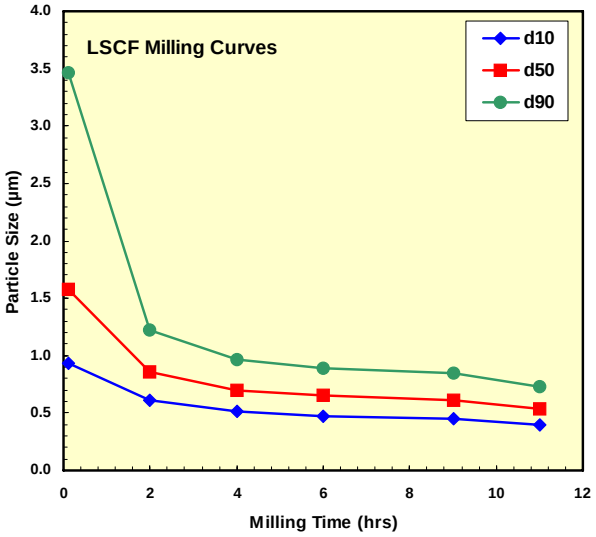

Figure 4

was selected using the Chi^2 and R calculations available in the LA-950 software. The plot in Figure 2 shows the change in fit parameters as the imaginary part of the refractive index was changed from 0 to 1.1. This approach resulted in choosing a value of 2.0-0.3i for the complex refractive index.

The LSCF powder was ball milled in water, using 1 mm YSZ beads for a total of 11 hrs. Figure 4 shows the progress of particle size reduction over the duration of milling as measured on the LA-950. The final median particle size was approximately 0.5 µm. A distinct narrowing of the distribution was also observed as shown in Figure 5. The analyzer was able to show the progress very effectively, even when milling was nearly complete and the changes in particle size were very small.

As mentioned earlier, the porosity of the electrodes is of major importance in the SOFC. The knowledge provided by the particle size analysis can be used to help tailor the porosity to the desired level. An estimate of the minimum porosity achievable for a particular distribution or combination of distributions can be made using particle packing calculations described by D.

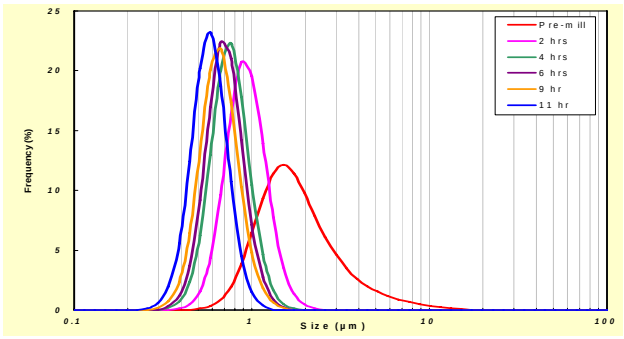

Figure 5

Dinger (Particle Calculations for Ceramists, 2001, D.R. Dinger Publishing, Clemson, SC). The calculations require the volume fractions of the individual size classes as given by the cumulative percent finer than (CPFT) distribution provided by the LA-950 analysis. The calculated porosity values apply to an unfired structure. After sintering, the actual porosity will be significantly lower.

The calculations show that a single, narrow, distribution will produce the most open structure while a broader distribution will produce a more densely packed structure. Table 2 shows that most of the PSD's produced by milling

would give a fairly open unfired structure with about 30 vol% porosity. Suppose our goal was to minimize the porosity in the final part, as is required for the electrolyte. As mentioned earlier, a broad distribution packs more densely than a narrow one. An extreme case would be if we used the distribution shown in Figure 6. The minimum possible porosity would then be 11.3%. One can further improve the packing by adding other, finer, distributions to the broad one. Calculations shown in Figure 7 indicate that combining the broad distribution with some of those produced by milling, can reduce the minimum achievable porosity to about 8%.

Table 2

Component	***Minimum Porosity (%)***
Pre-Mill	27.2
2 hrs	31.9
4 hrs	32.2
6 hrs	32.1
9 hrs	32.4
11 hrs	32.5

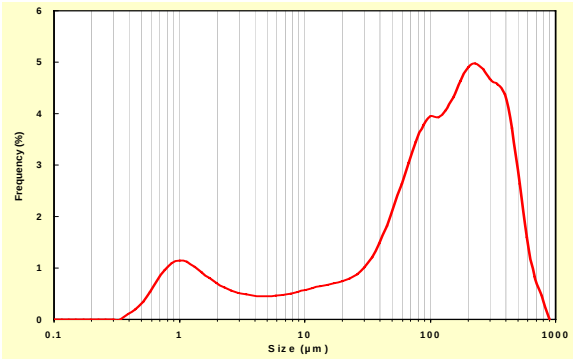

Figure 6

Conclusion

In any ceramic powder application, the particle size distribution is critical to product performance. In solid oxide fuel cells, PSD determines the final pore structure, which has important implications in the electrochemical performance of the cell. Fortunately, the fuel cell engineer, armed with accurate information about the size distributions of the powder, can tailor the final microstructure of the materials.

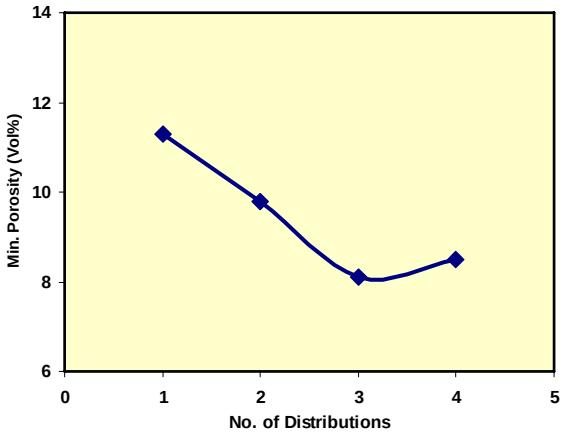

Figure 7

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