Manufacture of LSM and GDC Thick Film Pastes for SOFCs in ISO 9001 Environment

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Abstract

The range of active materials used in SOFC cell fabrication has grown rapidly over the last several years. Availability of these materials in the desired form (tape, paste, etc.) is crucial for the timely development of more efficient and robust SOFC structures. Equally important is the dependable supply of these products with consistent properties. Lot-to-lot variability must be controlled tightly to achieve reproducible cell performance. These objectives can be achieved more readily through product development and manufacturing in an ISO 9001 environment. This paper discusses the successful development, scale-up, and manufacture of a wide range of thick film paste compositions for SOFC applications.

Introduction

Most SOFC cell components can be readily fabricated from thick film pastes of the appropriate functional materials. Thick film paste categories manufactured by ESL include electrolytes, cathodes, anodes, current collectors, interconnects, and cell-stack sealants. Within each paste type, a wide range of compositions, including custom materials supplied by customers, has been manufactured. Vehicle systems are chosen and developed to provide stability and desired printing characteristics. Some typical products include paste compositions based on 8YSZ, GDC, 8YSZ+LSM, LSCF, 8YSZ+NiO, NiO, and LCC.

Formulation of thick film pastes requires mixing functional powders with organic liquids. The choice of organics is important for the printing and firing processes. Print characteristics such as thickness and thickness uniformity are important for large area prints required for cathode and electrolyte applications. Functional properties depend on proper dispersion and firing characteristics. Dispersion of sub-micron powders may be enhanced by the addition of appropriate wetting agents. Burn-out should be clean and free of residual carbon. If the paste is to be co-fired with green tape, interaction of the wet print with the tape substrate must be minimized.

Thick Film Paste Materials System

Cathode Pastes.

Compositions required for cathode applications must perform two main functions after firing. They must be catalytic to the transformation of oxygen molecules to oxygen ions. They also must be electrically conductive in oxidizing atmosphere at high (650-900°C) temperatures. The fired cathode must also retain enough porosity to insure gas-flow to and from the electrolyte. Oxygen, in the form of air must traverse the cathode while being transformed to oxygen ions, which diffuse through the electrolyte to react with the hydrogen and carbon monoxide on the anode side. The cathode paste must have a structure, which ensures this transformation while retaining its porosity and electrical conductivity. Powder morphology, particle size, and chemical integrity are all important properties that must be carried through the process of manufacturing the thick film paste.

Anode Compositions.

Anode pastes have similar requirements. The anode, typically reduced NiO in a NiO-YSZ composite, provides the catalytic action to reform the fuel gas to hydrogen and carbon monoxide. Electrical conductivity and porosity of this structure are also critical. An important SOFC configuration being the anode-supported cell, mechanical strength of the anode structure must be high enough for cell stack assembly. The addition of YSZ to the anode structure also adjusts the coefficient of thermal expansion (CTE) of the structure to enhance stability during thermal cycling. The ratio of metal to ceramic, with the possible inclusion of a fugitive pore former, will determine the efficient functionality of the anode. Anode pastes must be formulated to satisfy all of these requirements. Excellent dispersion and stability of these phases in the paste is required to insure optimum performance of the composite fired anode.

Electrolyte Compositions.

Although most electrolytes are formed from tape cast YSZ, electrolyte pastes are also used in some cases. This element of the cell must be dense, thin, uniform in thickness, and be completely free of connected porosity to insure optimum functionality. Eight mol percent yttria is most typical, but high ionic conductivity may be compromised to enhance strength with lower levels of yttria. Yttria may be replaced with Scandia to increase ionic conductivity at lower operating temperatures. Other electrolytes, including gadolinia doped ceria may also be formulated.

Interconnect Materials.

Thick films are also used in the interconnect region of the cell as current collectors. These must be formulated to insure a fired structure that can withstand the high temperature operating conditions in both oxidizing and reducing atmospheres as well as the thermal cycling required in most applications. Platinum inks work very well as current collectors, but are expensive. Replacement of platinum with lower cost alloys and perovskites, is the focus on many ongoing R&D programs. These include doped chromites such as LCC and LSCC.

Stack Seals.

One of the most challenging technical aspects of stack building is the formation of a robust seal between cells. Electrical insulation must be retained at operating temperatures in both oxidizing and reducing atmospheres after thermal cycling. Mobile applications of fuel cells may require tens of thousands of cycles. Even stationary power supplies will require hundreds of thermal cycles. The seal materials must match CTE of the gas manifolds if they are to survive these cycles. Thick film process offer the ability to inexpensively and reproducibly formulate these compositions. Many glass and glass ceramic compositions are being developed, which survive increasing number of thermal cycles.

Flexible Compositions

A major advantage of formulating thick film paste compositions is the ability to modify the composition even after the paste is made. Starting from end members, virtually a continuous series of intermediate compositions can be made by simply blending multiple end members. Another benefit of using paste materials is that even very small quantities of rare raw materials can be converted to pastes for evaluation purposes.

Paste Manufacturing Quality System

LSM and GDC thick film pastes for solid oxide fuel cells are being developed in laboratories all over the world. As new formulations are developed, evaluated, and improved, it is important to be able to reproduce them. An ISO 9001 management system helps ensure that this happens. Unfortunately, the disciplines of ISO 9001 do not exist in most laboratories. Where ISO 9001 certification is in place, the use of documented formulas and procedures is required. Documentation is developed with the initial development of any new product or process. Any changes that are made during the development process are tracked and documented.

Raw Materials Handling.

The process starts with the characterization of raw materials. Intermediates and final product properties are monitored as part of the process. Control charts are maintained for each measurement and are used to set meaningful specifications and monitor the suitability of raw materials. Measurement techniques are documented and gage repeatability and reproducibility (Gage R&R or GRR) studies are performed. Statistical Gage R&R studies determine the within-system and between-system measurement variation for a given measurement technique. Gage R&R studies enable us to minimize the measurement variation and ensure that measurements are meaningful. Control charts for average particle size and powder surface area for an LSM type powder are given in Figures 1 and 2, respectively.

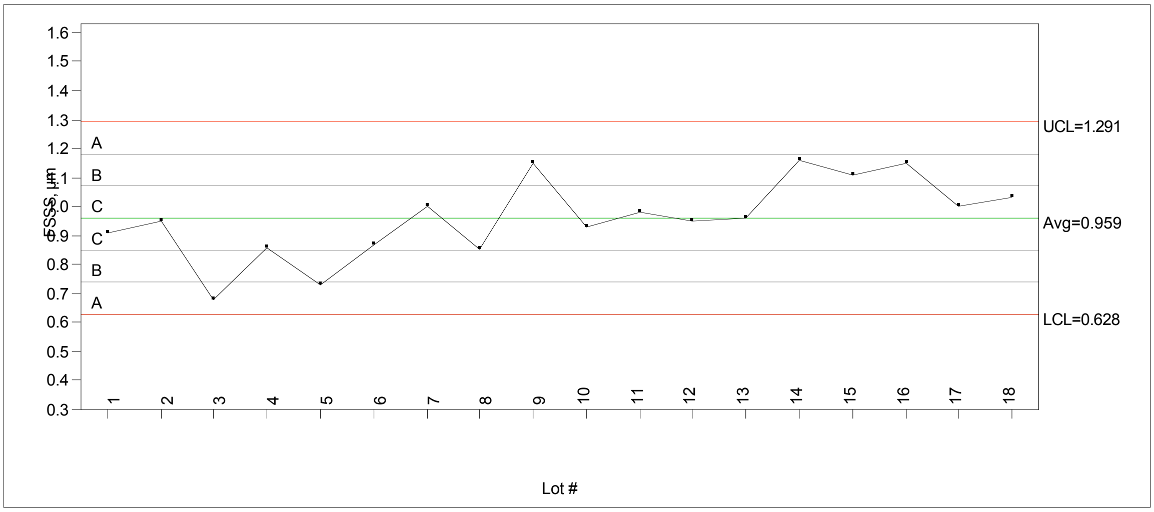

Figure 1. Control chart for the average particle size of an LSM type powder

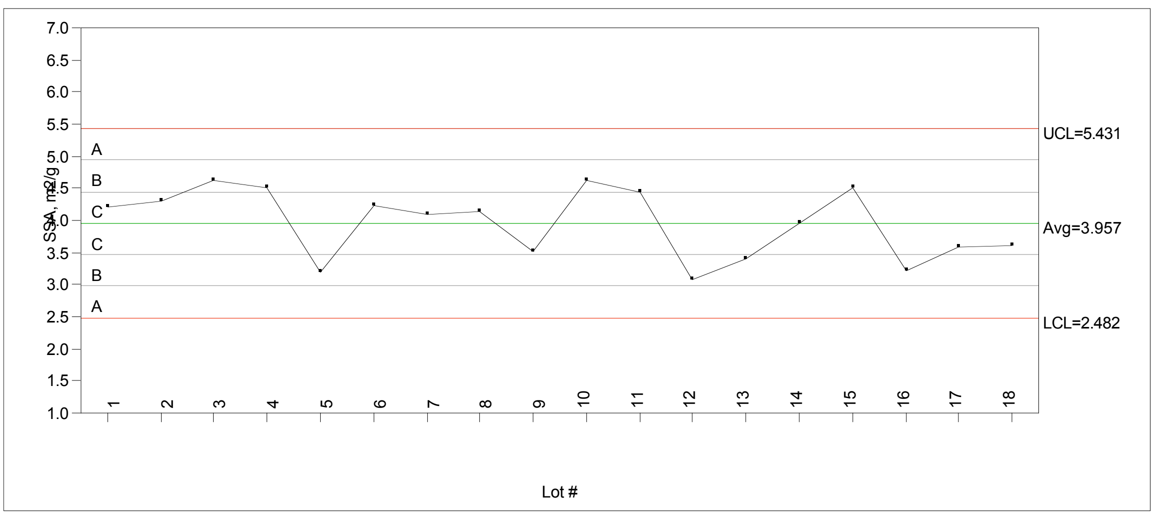

Figure 2. Control chart for the average surface area of an LSM type powder.

Control Systems for Paste Manufacturing.

The manufacturing process starts with the characterization of raw materials and continues through intermediates to finished products. The flow of materials is controlled, tracked, and documented throughout the manufacturing cycle. This applies equally well to new product development, facilitating ease of scale-up and subsequently an orderly and timely transition to manufacturing. Control charts are developed and maintained for all paste parameters measured. Rigorous control of paste properties results in consistent printing and firing characteristics including thickness uniformity, fired density, and fired porosity, where appropriate. Control charts for two common but critical paste parameters, viscosity and solids content, for a product typical of LSM pastes are presented below.

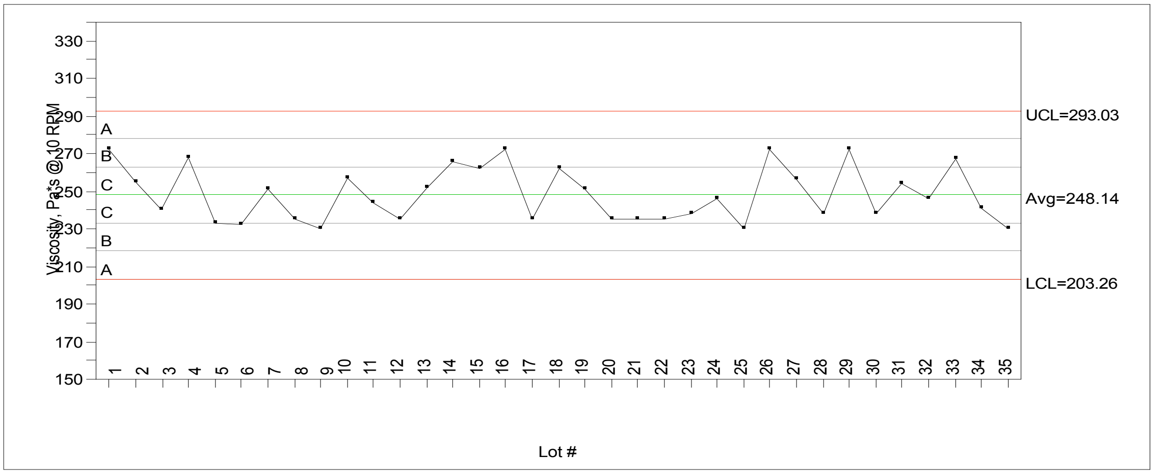

Figure 3. Control chart for the viscosity of an LSM type paste.

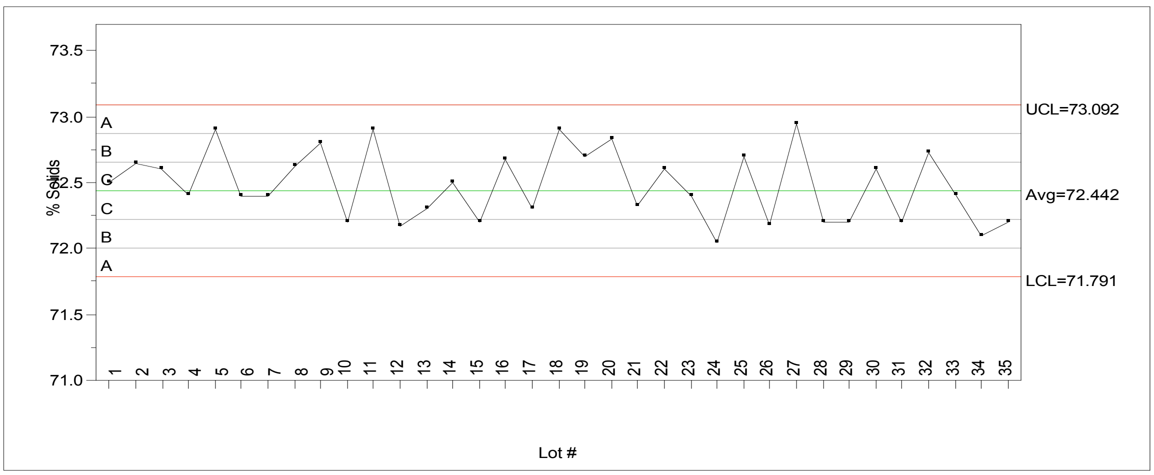

Figure 4. Control chart for the solids content of an LSM type paste.

Conclusion

Practicing well established ISO 9001 total quality principles enables ESL to develop and manufacture high quality thick film paste products for SOFC applications consistently and economically.