MANUFACTURABILITY OF VERY THIN ELECTROLYTE TAPES FOR SOFCs IN AN ISO 9001 ENVIRONMENT

A. H. Feingold, R. L. Wächters, M. Heinz, E. Twiname, Z. Topka
ESL Electro-Science, King of Prussia, PA, USA

J. Whitmarsh
ESL Europe, Reading, UK

ABSTRACT
Commercial possibilities of solid oxide fuel cells improve with technological progress. However, success of this technology depends on bringing economic advantage to market and profit to materials, cells and systems manufacturers. Tape casting, a well-established technique, currently provides materials for several fuel cell programs. Anode tapes for anode-supported cells and electrolyte tapes for anode- and electrolyte-supported cells are manufactured in laboratory and large prototype volumes. Dense, crack-free, electrolyte tapes provide the high ionic conductance required for cells to function. Efficiency and area-specific resistance are related to electrolyte ionic resistivity. Thin electrolyte tape, capable of meeting overall system requirements is therefore desirable. The technological advantage, however, presents a manufacturing challenge. This paper discusses the ability to cast YSZ tapes that fire to full density in thicknesses <12.5 μm and equipment and procedures required to make these measurements in prototype and manufacturing environments. Manufacturing under ISO 9001 conditions ensures reproducibility in the laboratory and eases scale-up to manufacturing. Incoming materials inspection ensures consistent powder properties such as particle morphology and surface area. Slurry viscosity and casting parameter limits control green tape properties. Green and fired thickness, and fired density measurements confirm quality. SPC charts of this data will be presented.

INTRODUCTION
Materials for solid oxide fuel cells are being developed in laboratories all over the world. As new formulations are evaluated, it is important to know that the good ones can be reproduced. An ISO-9001 documented system is aimed at ensuring that this will happen. Unfortunately, ISO-9001 does not exist in most laboratories. Formulas and process procedures are part of the ISO-9001 system. In a manufacturing environment where ISO-9001 certification is in place, it is required that these documentation procedures are followed. This starts with the initial development of any new product or process. Changes that are made as the development progresses are tracked and documented.

The process starts with characterization of the raw materials. Intermediates and final product properties are monitored as part of the process. Control charts are maintained for
each measurement. Measurement techniques are documented and gauge repeatability and reproducibility (R&R) testing ensures that measurements are meaningful.

The tapes used for solid oxide fuel cells can be manufactured economically under these conditions, because formulations and processes are reproducible and waste is correspondingly minimized. Scale-up issues are also minimized (1) and economies of scale can apply to larger lots of materials required for prototyping cells and stacks.

The tapes used for the electrolyte function present an unusual challenge. Cell efficiency depends on the properties of this tape, since a small tape defect may harm or destroy the overall cell. Internal resistance of a cell determines the ionic conductance and consequently the efficiency of electron production (2). Since resistance is a product of ionic resistivity and thickness, these properties are the focus of many development programs (2). A variety of chemical formulations have been evaluated in efforts to increase conductivity at lower stack temperatures, which would lower the cost of materials. Although a variety of electrolyte compositions have been cast at ESL, the focus of work is on tape thickness. Fired electrolyte thicknesses as low as 6 to 8 μm have been attained with these tapes. The tapes described in this paper are cast in the range of 10 to 20 μm green (unfired). ESL has routinely manufactured tapes in this thickness range and ISO-9001 manufacturing documentation has been established to ensure control consistency from lot to lot and with scale-up.

The techniques used to cast these tapes and the procedures used to characterize and document the raw materials, intermediates and final product are described.

THE NEED FOR THIN TAPE

The basic operation of a solid oxide fuel cell is as follows. Hydrogen (and carbon monoxide) are reduced at the anode \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \) yielding two electrons to the external circuit. At the cathode, oxygen becomes ionized by picking up two electrons \( \frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^2^- \). The electrons travel through the external circuit to the anode to allow the hydrogen reduction. The rate of reaction is limited by the ability of the oxygen ions to traverse the solid electrolyte to complete the circuit at the anode, reacting with hydrogen ions \( 2\text{H}^+ + \text{O}^2^- \rightarrow \text{H}_2\text{O} \) to form water. Cell functionality depends on ionic conduction of \( \text{O}^2^- \) through the electrolyte. If electrons penetrate the electrolyte (electrical conductivity), the flow of electrons through the external circuit would be short circuited. Therefore the electrolyte must have high ionic conductivity and minimize electrical conductivity. Furthermore, for high efficiency the electrolyte must have a dense microstructure to minimize penetration of un-ionized gases which would reduce efficiency.

The electrolyte requirements can be summarized as follows:

- Compositional integrity and thinness for highest ionic conductivity with minimal electronic conductivity
- Density to minimize gas penetration
- Large area to maximize current capacity
- Strength to resist thermal and mechanical shock

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The composition of the electrolyte will determine the ionic conductivity. Although yttria stabilized zirconia is not the most conductive composition reported, its high electrical conductivity at operating temperatures of 600 to 1000°C contributes to its usefulness. It is desirable, however, to operate cells in the lower end of this temperature range to extend cell life, reduce thermal stress, improve reliability and reduce cost. For example lower cost metallic interconnect structures can be used below 800°C. This creates an additional burden on the electrolyte, since ionic conductivity decreases exponentially with decreasing temperatures (T).

$$\sigma \sim (1/T) e^{(-E/RT)} \quad [1]$$

where E is the activation energy for ionic diffusion. While electrolyte thickness of 50 to 250 µm are useable at temperatures above 800°C, thickness must be reduced to the 5 to 20 µm range in order to operate efficiently at temperatures below 800°C (3). This follows from the fact that area specific resistance can be reduced by reducing electrolyte thickness (t).

$$R = (1/\sigma) t \quad [2]$$

It is therefore desirable to economically and reproducibly use the thinnest tape feasible.

**RELIABLY MAKING THIN TAPE**

Methods of casting ceramic tape depend on whether the tape is to be thick, intermediate or thin. Each method has similarities with the others but also involves specific techniques, formulations and equipment. These three thicknesses are generally understood to be; < 50 µm, 50 to 1000 µm and >1000 µm (4). Tapes in the middle range include MLCP, electrode-supported SOFC and LTCC, while thick tapes are more commonly used for armor, substrates or other structural applications. Manufacture of thin tapes (~< 50 µm) has until recent years been the realm of passive components alone; MLCC, MLCI, etc. The manufacture of these thin tapes entails manufacturing and handling challenges. Casting variables such as dispersion and thickness variation become magnified in importance.

Thin tapes require greater dispersion of inorganic particles. While this is true of most wet ceramic processes, this need becomes more critical as tape thickness decreases in order to minimize structure defects stemming from even low levels of agglomeration. Achieving excellent dispersion becomes more difficult due to the need for extremely fine particles, with correspondingly high surface area (4), in thin tapes. Submicron or “nano-scale” powders are known for their tendency to agglomerate. Particle size must decrease to ensure a packed particle bed. This is necessary to increase structure uniformity in both green and fired states, minimize or negate through-layer defects, homogenize densification shrinkage and increase the strength of the layer after sintering (4).

Thin tape requires enough green strength per unit of cross-sectional area to maintain integrity through device assembly. Building this strength into a high surface area particle bed requires a delicate balance between dispersion, strength, green density and viscosity. Controls must be established and maintained for consistency.
Many equipment-related demands also accompany the manufacture of micron scale tapes. Simple tasks such as tape thickness measurement as an in-process control check must be performed on more sensitive and accurate equipment than is typically found in a production area. For green tape thickness in the range of 12.5 μm, production floor measuring equipment must have accuracies in the single micron range. Commercially available precision milled or surface ground casting heads (doctor blades) often have flatness tolerances no better than 2.5 μm and up to 5 μm after use. Solid granite precision casting surfaces may only be certified flat to 8 μm. Polymer carrier films claimed to have been processed in clean rooms have been seen to include static related debris larger than 8 μm. These mechanical factors and additional factors such as web speed uniformity, head pressure repeatability, slip homogeneity, lot to lot repeatability of casting slips and in-depth operator training become key process variables as layer thickness decreases to <50 μm (4).

PROCEDURE AND RESULTS

The procedures and controls described above were put to use to cast very thin (10-20 μm) electrolyte tape. YSZ powders were obtained from several sources to determine the parameters required to cast consistent tapes. Incoming powders were characterized by measuring surface area, particle size distribution and other parameters. Powder lot records were maintained so that cast and fired tape properties could be traced back to the original lots of powders and their properties. The submicron YSZ powders used had surface areas in the range of 8-10 m²/gm.

Slurries were formulated using phosphate free dispersants and solvents that could be used safely in manufacture. This precluded the use of toluene. PVB binder systems were chosen which provide good strength for handling thin green tapes. Formulations included enough binder to ensure adequate laminating characteristics. The YSZ powders were dispersed for 24-48 hours before binder is added. Dissolution milling followed for an additional 24-48 hours. Viscosity of the dispersed powder slurry is monitored to determine that agglomerates of the high surface area powders are adequately broken up. After complete dissolution of the binder, viscosity was adjusted to a range, which is consistent with practical casting parameters.

The casting slurry was then de-aired to remove dissolved bubbles and finally filtered before it is fed into the doctor blade reservoir. An initial set-up of the doctor blade height was adjusted after the dry green tape came off the caster and was measured to assure that the thickness was within the control range. The leading part of the cast was discarded after this adjustment is made. Drying parameters and casting rate were optimized for the slurry composition to maximize throughput. The tape was periodically monitored for thickness along the length and across the width of the cast. Figure 1 shows thickness data taken on a 250 meter (~800 feet) cast of electrolyte tape. Each point represents the average of four points taken across the 8 inch width of the cast. This lot (number 8 in figure 2) is typical of the data obtained on all the thin tape casts shown in figures 2 and 3. The dried tape was then taken onto rolls at the end of the caster. Each cast was re-rolled on a light table for visual inspection and additional thickness measurements.
Figures 2 and 3 are charts of green tape thickness obtained for two thicknesses of green tape. Figure 2 shows data obtained from nine separate lots of tape cast to a target green thickness of 14.5 μm. The target thickness for the five lots of tape shown in Figure 3 is 12 μm.
Figure 4 shows data obtained for green density for the five lots of electrolyte tape shown in figure 3. Green density is an indication of solids loading and powder dispersion in the casting slurry. High green density led to lower shrinkage and a more consistent fired tape. All measurements were done using procedures, which had been certified to pass gauge R&R. This ensured acceptable measurement variation among operators.

These electrolyte tapes attained density >97% of theoretical when fired at 1450°C for 2 hours. For anode-supported cells, the electrolyte tape was typically laminated to the anode support structure and co-fired with the anode tape. Our customers reported that the resulting fired electrolyte tape was free of leaks when subjected to helium leak detection.

![Figure 4. Green density.](image)

**CONCLUSIONS**

The ability to consistently cast very thin electrolyte tape in a documented prototype and production environment has been demonstrated. This allows the developers of solid oxide fuel cells to do experiments with consistent materials. The data presented in this paper is for YSZ tapes. Other electrolyte materials have been cast with similar controls and specifications. ISO-9001 compliance ensured consistency from incoming inspection of raw materials to final tape and cell properties.

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