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Tape casting of lanthanum chromite for solid oxide fuel cell interconnects

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ABSTRACT

A method, based on tape-casting, is developed for the manufacture of ceramic interconnects for SOFCs. The development of an optimized process is shown with a discussion of the effects on the precursor-slurry quality and viscosity of, among other things, the concentrations of ammonia, binder and solid particles. Furthermore the effects of some processing modifications, such as the drying rate in the tape casting machine, the speed of the transport band and the doctor blade height on the quality (density and homogeneity) of the green tapes and the finished product are discussed. Improving the degree of dispersion of the primary particles in the slurry was found to make possible improved densification and quality of the thick plates produced as did reducing the drying rate of the wet tapes during the casting process.

1. Introduction

Solid oxide fuel cells (SOFCs) play an increasingly important role in fuel cell technology due to their high efficiency. Efforts to model their working in detail have been carried out recently. Ho et al. (2009), for example, studied the transport processes taking place in solid oxide fuel cells and on basis of this constructed a model for their operation. They found that the diffusion algorithm in CFD packages could be used for the transport of charge in the cells *if this transport was in steady state*, otherwise not. Janardhanan and Deutschmann (2007) studied numerically reforming anode-supported solid-oxide fuel cells running on CH_4 finding that internal reforming, as one might expect, leads to a drop in the temperature at the inlet to the cell. However, a number of challenges remain before SOFCs can be utilized commercially on a large scale. Many of these challenges, but also many of the advantages of SOFCs, are related to the relatively high operating temperatures of this type of fuel cell.

One of the key components of SOFC power conversion installations where there is still scope for significant improvement are the interconnects. The interconnects in planar SOFC installations have three main purposes: to connect the individual cells in a stack electrically, to keep the fuel and the oxidising gas separate, and to separate the cathodes and anodes of adjacent cells in the stack.

1.1. Interconnects

It is essential that interconnects fulfil the following conditions throughout the very wide range of temperatures (25–1000 °C) and chemical conditions that they are exposed to:

- Excellent electrical conductivity, preferably in excess of 1 S/cm.
- Impermeable to both fuel and oxidizing gases, which is achievable through materials with low porosities ($< 6\%$) or high densities relative to the theoretical density ($> 94\%$).
- Stable, both chemically, microstructurally and mechanically.
- Compatible thermal expansion coefficient with both electrodes and with the electrolyte.
- Good thermal conductivity (> 5 W/mK) in order to transport heat produced in the anode to the cathode, increasing the efficiency of the latter.
- Easy and low-cost both in terms of materials and manufacturing.

Two types of materials are used for interconnects, ceramics and metals. Both have advantages and disadvantages. The choice depends on the design, the operating temperature, the required service life and material and fabrication costs. In general, metallic materials tend to be used more for operating temperatures below 800 °C, whereas operating temperatures above 800 °C, where the internal resistances in the cell are much lower and the efficiency of the electrode catalyst is higher, require ceramic interconnects.

Smith (2005) found that the relative density of ceramic interconnects is very important for their mechanical strength. A pore or a flaw in the material may grow in a process akin to fatigue in metals due to mechanical or thermal stresses, eventually resulting in failure.

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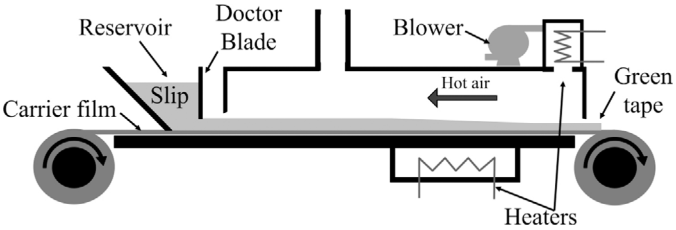

Fig. 1. Schematic illustrating the tape-casting process.

1.2. Tape casting

Tape casting is also referred to as doctor blading and knife coating. It is normally used to create thin ceramic layers, but in this work the focus is to create thicker plates. The process involves a number of steps:

- **Mixing**: The components are mixed together to break agglomerates in the powder, to obtain a homogeneous suspension.
- **Forming**: This step, illustrated in Fig. 1, is the actual tape casting process.
- **Drying**: The wet tape is dried using heaters in the tape casting machine to produce green tapes.
- **Firing**: The green tapes are sintered in a controlled heating process, unwanted additives are removed.

The effects of the rheology of the suspension on the quality of the produced tapes in aqueous tape casting has recently been the subject of some interest within the materials processing community. Joshi et al. (2002) studied two rheological models for the suspensions used for ceramic tape casting. Olhero and Ferreira (2005) studied the rheological properties of aqueous concentrated AIN suspensions in the presence of a sintering aid with a view to obtaining crack-free tapes.

The production of lanthanum chromite interconnects for SOFCs has been studied extensively from the production techniques for the starting powder, over stoichiometric manipulation to enhance material properties, to the sintering procedures with the aim of lowering the high sintering temperatures. However, research on tape casting of lanthanum chromite is very limited, and only a couple of these studies use aqueous suspensions. Previous investigations of tape casting are presented in this section, emphasizing the challenges of formulating the correct slip composition.

Murphy et al. (1997) investigated the effects of various process components for tape casting suspensions of $La_{0.7}Ca_{0.3}CrO_3$. The powder was produced by a continuous combustion synthesis. The effects of three dispersants were studied by zeta potential measurements and rheology measurements. Particle dispersion was better using 1 wt.% of aliphatic phosphate ester. After a formulation was achieved based on dispersant, the effect of calcination temperature was studied. Measurements demonstrated that the particle size increased with calcination temperatures due to coarsening. The binder content of the slurry was selected on basis of tape quality. Finally, the slurry solid loading was selected to achieve a viscosity in the range of 200–400 mPa s. Tapes were casted, dried for 10 h, and sintered at 1300 °C. Relative densities of 97.8% were achieved.

Setz et al. (2011) studied the tape casting and sintering processes for a doped lanthanum chromite powder ($La_{0.8}Sr_{0.2}Cr_{0.92}Co_{0.08}O_3$). The powder was produced by combustion synthesis and characterized. The zeta potential was also measured for suspensions prepared with different concentrations of dispersant (polyethylene glycol), 1 wt.% dispersant resulted in the best dispersion. The solid loading was selected based on rheology measurements whereby the Krieger–Dougherty rheological model was used. To select the binder and plasticizer (B/P) content, different ratios B/P were studied together with the tape casting parameters. The effect of the doctor blade height, the casting speed and the B/P ratio was evaluated in terms of quality of the produced tapes. Green tape density was 2.1 g/cm^3. The plates were sintered at 1600 °C for 4 h leading to a density of 97%.

Tai and Lessing (1991) studied both tape casting and sintering of strontium-doped lanthanum chromite. The powder was produced by a modified Pechini method and characterized. The slurry composition is presented; unfortunately no procedure for its optimization was reported. Phosphate ester was used as dispersant at a concentration of 0.2 wt.%. The solids loading was 61.5 wt.% which gives rise to an extremely high viscosity of 3000–5000 mPa s. The binder content was chosen upon tape quality.

Sintered interconnects are usually machined to realize the dimensions and the channels. Tai and Lessing (1991) presented an alternative method, in which the channels were embossed into a green tape. The tapes were sandwiched between two plates of Cr_2O_3 during sintering with the objective of saturating the air with CrO_3 gases, and prevent chromium condensation in the particles' surfaces. The interconnects were sintered at 1670 °C for 7 h and a density of 93.5% was achieved.

The previous studies share the same way to formulate a slip. First, dispersant content is determined as that giving the highest zeta potential, and lowest viscosity, which is also the pH levels that result in better particle repulsion. Secondly, the binder content is set in light of the quality of the tapes obtained. Lastly the solids loading is determined by the required slip viscosity, which varies significantly between the studies. Viscosity requirements are set by the required thickness of the tapes, as higher viscosities can produce thicker tapes.

2. Objectives of this work

The focus of the work described in this article is to develop and test a method, based on tape-casting, for production of ceramic interconnects for SOFCs.

The development of experimental procedures in this paper was partly based on the studies mentioned in the previous section. The objectives are the same, namely to achieve good particle dispersion, processable viscosity and good tape quality. However, since the objective in this work is to form thick plates rather than the thin ones formed in previous studies, the order and the details of the procedures are different in this study.

Each successive step of the procedure has been analyzed using the appropriate methods and optimized so as to point the way to an optimal over-all process.

3. Analyses and development of methods

A flow chart illustrating the over-all process is shown in Fig. 2. The experimental methodology was created and developed by the authors.

An initial short milling stage is intended as a mixing process, whereafter two real milling stages of the powder with binder and defoamer are carried out to disperse the powder as much as possible into its primary particles. The suspension is then allowed to deair for 15 min. A rheological characterization is carried out in a rheometer, whereafter the suspension is charged to the tape casting machine and the green tapes produced. The green tapes are then characterized in terms of their quality, checking them for any cracks and they are laminated to produce plates that are sufficiently thick for the production of interconnects. The quality of the lamination is checked, and finally the resulting thick plates are sintered and subjected to a final inspection.

3.1. Characterization of the powder

The starting material is a commercial powder of calcium-doped lanthanum chromite ($La_{0.8}Ca_{0.2}CrO_3$) from Pyrox, France. The composition is given in Table 1.

This powder is currently used in industry to produce interconnects by a process known as press and sinter.