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Aqueous tape casting of yttria stabilised zirconia using natural product binder

F. Snijkers*, A. de Wilde, S. Mullens, J. Luyten

Flemish Institute for Technological Research (Vito), Materials Technology Boeretang 200, B-2400 Mol, Belgium

Abstract

A new and simple tape cast process has been developed for e.g. the fabrication of YSZ-electrolyte for solid oxide fuel cells (SOFC's). The method is environmentally friendly since it is water-based and uses a natural compound as a binder. The tape cast suspension was formulated taking into account a maximal solids loading, a minimum of organic compounds, colloidal stability, rheological and wetting properties. Green sheets of variable thickness (50–400 μm) have been prepared. After sintering, dense and defect-free electrolyte material, as required for SOFC's, was obtained. The microstructure and the surface of the sintered sheet material were characterised with FESEM.

Keywords: Ceramic processing; Fuel cells; Membranes; Tape casting; ZrO_2

1. Introduction

In the last decade, much effort has been spent on water-based casting processes that use water and natural products as constituents in order to replace toxic solvents and binders.[1–8] In line with this evolution, a new and simple tape casting process has been developed. Tape casting is a well known colloidal shaping technique for thin ceramic components, that are often used in electronic applications. The technique is also used for the production of substrates or components like the electrolyte or the anode for solid oxide fuel cells (SOFC's). The thickness of tape cast products are typically in the range of 20 μm to a few millimeters. The technique often uses a suspension containing a binder, that is either solvent- or water-soluble. An overview of binders used in tape casting processes is presented in ref 9. A typical example of an organic solvent-soluble binder is poly-vinyl butyral, examples of water-soluble binders are poly vinyl alcohol, methyl cellulose or starches.[1,9] Few other natural binders used in a tape casting process than the fore-mentioned are known of.[10] The combined use of a natural compound as a bio-binder and water as a solvent will result in an even more environmentally friendly tape casting process.

From a point of view of process control, solvent based tape cast processes are considered to be better a choice over water-based tape cast processes.[11] However, environmental concern has stimulated the interest in water-based tape casting processes.

The starting suspension for tape casting basically contains the ceramic powder or powder mixture as the functional phase, solvent, the additives (anti-foaming, dispersing agent, surfactant...), the binder and one or more plasticizers. In order to achieve complete dissolution of the hydrocolloid, the slurry is heated to a certain temperature. After de-aerating, the slurry is tape cast with a so-called doctor blade on a carrier film. The properties of the bio-binder result in easy to handle tapes. In further steps the tape is removed from the carrier film, followed by drying, thermal treatment to remove organics compounds from the green product, and sintering. If required, further shaping, calendaring or lamination could be done in between drying and calcination. An overview of the tape cast process flow is presented in Fig. 1. In this contribution specific aspects of aqueous tape casting of YSZ, a well known electrolyte material for SOFC's are discussed.

From the work on bio-binder-based gel-casting processes, gelatine was selected to fulfil the role of binder in a water-based tape cast process. In this study we focus

* Corresponding author. Tel.: +32-14-335665; fax: +32-14-321186.
E-mail address: frans.snijkers@vito.be (F. Snijkers).

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on the potential use of gelatine as a water-soluble binder in tape cast processes.

2. Experimental

2.1. Materials

Yttria (8 mol%) stabilised zirconia (grade TZ-8YS) with a specific surface area of 6.9 m^2/g and d_{50} of 0.3 μm (Tosoh, Japan) was used as ceramic powder. Deionised water was used as the solvent. Gelatin (Cryogel 220/440 from PB Gelatins, Belgium) was selected as binder and polyethyleneglycol (PEG 400, Merck Germany) and linseed oil as plasticizers. A fluorosurfactant FC-4432 (3M, Zwijndrecht Belgium) was added, in order to adjust the wetting properties of the suspension.

Dispersion was promoted by adding a small amount of Darvan C as a dispersing agent (ammonium salt of poly(methacrylate), supplied as a 25 wt.% solution in water, RT Vanderbilt, Norwalk, CT, USA), thus controlling the pH of the suspension between 7.5 and 8. Tape casting was done with moving single doctor blade on mylar substrate film with a surface energy of 60 mN/m, with speeds that were varied in the range of 0.25–2 cm/min.

2.2. Characterization

Zeta-potential measurements were done with a Coulter Delsa 440. The rheological behaviour of the binder solutions and the ceramic suspension was measured with a rotary rheometer (Haake RS 100, Germany) using concentric cylinders as a measurement sensor, allowing a precise control of temperature and preventing evaporation of solvent. The wetting properties of a water-based system with bio-binder were assessed by measurement of the surface tension with the ring method apparatus (Krüss GmbH, Hamburg, Germany). The characterization of both green and sintered tapes focussed on the homogeneity by visual inspection on a backlight table and on optical microscopy and FESEM (Jeol JSM-6430F) to investigate the microstructure.

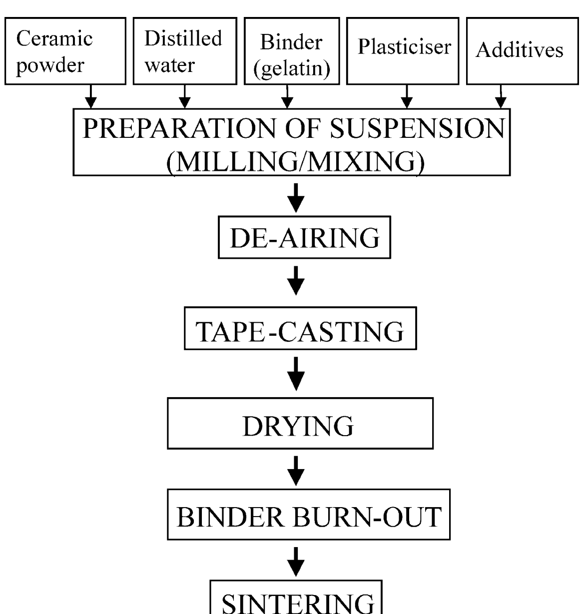

Fig. 1. Process flow for tape casting 8YSZ with natural binder.

3. Results

3.1. Suspension stability and rheology

The zeta-potential of TZ-8YS powder has been measured as a function of the pH. The iso-electric point was found to be around pH 5.4. For this reason the pH of the tape-cast slurries was controlled around pH 7.7 by adding 0.5% (as active material with respect to the YSZ-powder) of dispersant to the suspension (Fig. 2). In earlier work,[2–5] the compatibility of gelatin with a range of pH's was checked for and it was found that gelatin could be used with pH's ranging from 3 up to 10.

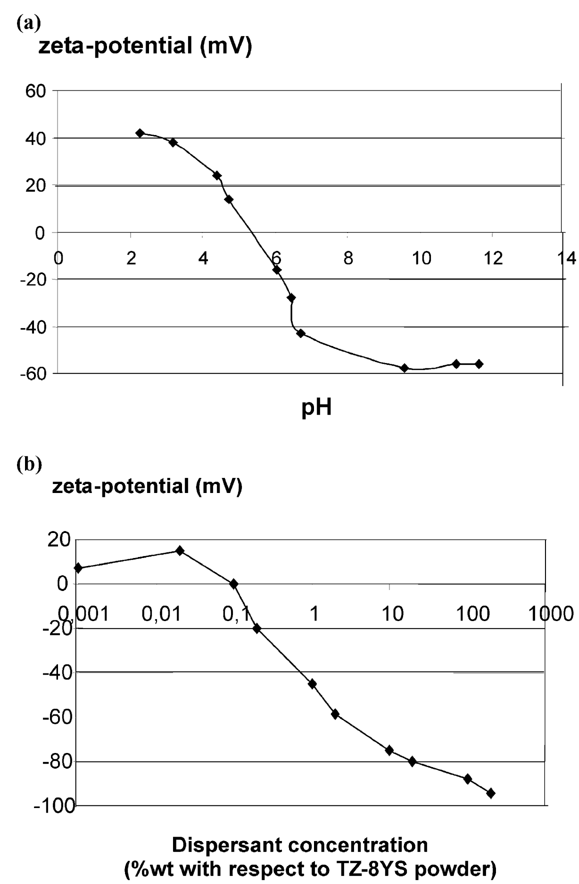

Fig. 2. (a) pH dependence of zeta-potential for TZ-8YS-powder; (b) dispersant-concentration dependence of zeta-potential for TZ-8YS-powder.

Fig. 3 clearly shows the pseudo-plastic behavior of a typical tape cast slurry. In addition to the usual temperature dependency of the viscosity, a slurry with gelatin as a binder will show a fairly steep increase of the viscosity with decreasing temperature, as a consequence of the gelling behaviour of the binder. The gelling mechanism of gelatin is formation of double helices by part of the biopolymer chains. These double helices are further stabilised by hydrogen bonds.[12] Because of the easy disruption of these interactions by heating, the gelling is thermally reversible. This means that casting is preferably to be done above the gelling temperature and that the temperature must be well controlled. For gelatin, the gelling temperature is typically around 30 °C. Some extra process control is considered necessary to meet this condition.

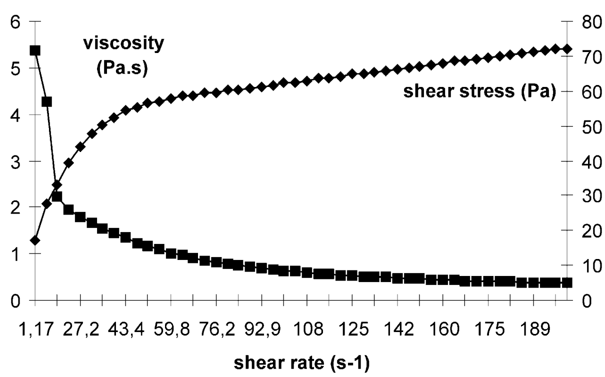

Fig. 3. Shear rate dependence of viscosity and shear stress for typical tape cast suspension with gelatin binder at 26 °C (decreasing shear rate).

3.2. Wetting properties

An important aspect of the tape casting process is the wetting behaviour of the substrate film by the ceramic suspension. Serious de-wetting problems were met with silicone-coated substrate film. In order to circumvent the de-wetting problems two measures were taken: firstly the substrate film was changed from silicone coated to uncoated substrate film. Secondly, a surfactant was added in order to reduce the surface tension of the suspension. This leads to acceptable wetting in combination with the possibility to easily separate the tape from the substrate film. The effect of gelatine concentration on the surface energy of water-gelatin solutions has been investigated, see Figs. 4a and b. The addition of gelatin to water already reduces the surface tension, but to obtain good wetting it is necessary to further add surfactants. At higher concentrations, little difference is observed between two different types of gelatin, yet at lower concentrations the 'cryogel'-type gelatin seems to reduce the surface tension more than 'low bloom' gelatin does.

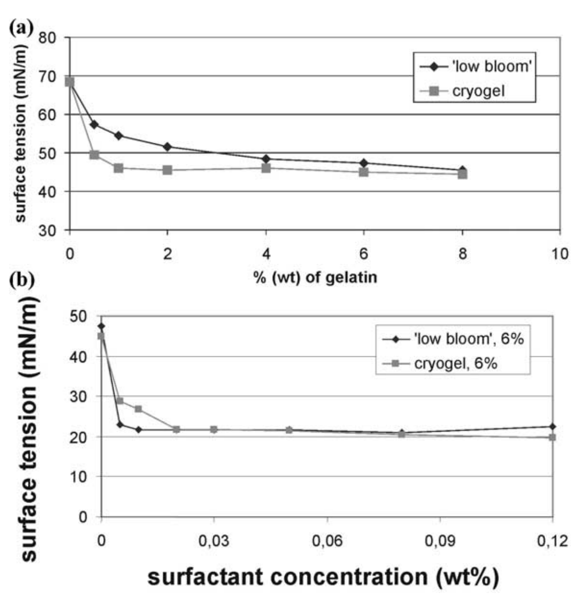

Fig. 4. (a) Effect of gelatine concentration on the surface tension of solutions of gelatin in water; (b) further reduction of the surface tension by addition of surfactant to 6% aqueous gelatin solutions.

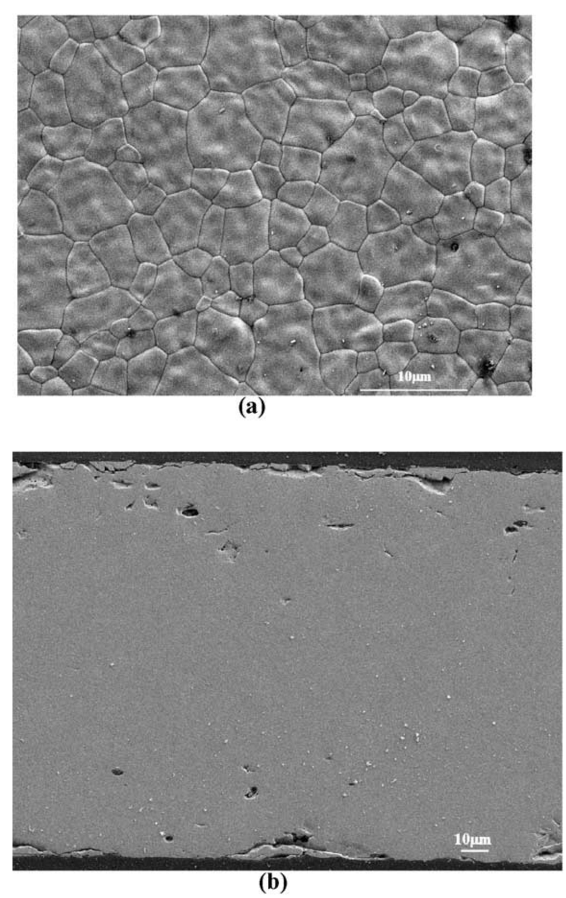

Fig. 5. (a) FESEM-picture of sintered ZrO_2-tape surface; (b) FESEM-picture of cross-section of sintered ZrO_2-tape.

3.3. Characterization of green and sintered tape

Fig. 5a shows FESEM-pictures of the typical microstructure of the surface of the sintered tape. Size of the grains are in the range of a few to 10 μm. Cross-sectioning of sintered YSZ-tape reveals that a fairly dense layer is obtained with only little closed porosity.

4. Discussion and conclusions

Water-based tape-casting with gelatin binder can result in an environmentally friendly method on the condition that it can be made a practical method. To this end, the features that are considered disadvantageous for water-based tape-casting with regard to organic solvent-based tape casting have to be considered.

Water has, in comparison with organic solvents, a rather high surface tension.[13] In this paper however it is shown that the use of the gelatin binder readily reduces the surface tension; yet the addition of a surfactant is required in order to bring the surface tension down to figures that apply to non-aqueous systems. It has also been demonstrated that a slip with a rheology appropriate for a tape cast process can be obtained. In addition the suspension formulation allowed a solids content as high a 66 wt.%.

A new and simple tape casting process has been developed for e.g. the fabrication of YSZ-electrolyte for solid oxide fuel cells (SOFC's). The method is environmentally friendly since it is water-based and uses a natural compound as binder. Green sheets of several thicknesses (50–400 μm) have been prepared. After sintering, dense and defect-free electrolyte material, as required for SOFC's, was obtained. The microstructure of the sintered material was investigated by means of FESEM.

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