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Microstructure, mechanical behavior and flow resistance of freeze-cast porous 3YSZ substrates for membrane applications

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ABSTRACT

Freeze-cast porous 3YSZ with different porosities were characterized as mechanical load carrying supports for oxygen transport membrane applications. Porosity influence on mechanical properties, i.e. elastic modulus and fracture stresses was assessed with biaxial ring-on-ring bending tests. The flow resistance was characterized in terms of the pressure drop using different gases to reveal the effect of the porous support on the accessing of the inlet gas flow to the functional dense membrane layer. Both properties were discussed in terms of the influence of porosity and pore structure, and compared with the properties of porous 3YSZ produced via pressing and sintering.

1. Introduction

Mixed ionic–electronic conducting (MIEC) ceramic-based membranes attract increasing attention as interesting cost-effective alternative means for oxygen production [1]. Two possible industrial applications for such membranes are oxygen supply in Oxyfuel power plants and the integration in catalytic membrane reactors [2]. Especially in the oxyfuel process, the use of these high temperature ceramic transport membranes promises lower losses in power plant efficiency compared to the cryogenic distillation and pressure swing adsorption industrial processes [3].

As stated by Wagner's equation [1,4], the flux through a dense membrane is proportional to the inverse of the membrane thickness. Therefore, for practical applications, where high oxygen fluxes are necessary, thin membranes are required to increase the flux of oxygen by minimizing the ion diffusion limitation. Recently, with respect to application relevant membrane designs, an asymmetric membrane consisting of a thin dense membrane layer supported by a porous substrate was suggested [5–7]. The aim of asymmetric membranes is not only to boost the gas transport but also to enhance the mechanical stability of the entire thin layer membrane structure, which therefore renders the mechanical properties of the porous substrate critical for the reliability of the whole component [6,8,9], hence being the focus of various recent studies [8–16]. The support engineering is then crucial and the substrate has to fulfill certain mechanical, microstructural and physio-chemical requirements, which are [17]: (i) to confer a good mechanical integrity on the porous support/dense top layer assembly and to avoid possible damage under harsh conditions, (ii) to minimize the pressure loss through the support in order to allow the membrane to operate at high flow rates and (iii) to provide a high mixed electronic and ionic conductivity and a high density of Triple Phase Boundary (TPB) where ion, electron and gas can meet for the oxygen reduction reaction. Indeed, due to the limited reaction site density at the interface porous support/dense layer, it is necessary that the porous support has a high TPB density, where the gaseous oxygen (in the case of O_2 separation) and the electronic and ionic conductive phases contact.

Current pore-forming techniques in the fabrication of porous ceramics utilize thermally fugitive compounds (polystyrene, carbon/graphite, etc.) to generate a variety of pore structures that are dependent upon the morphology and packing of these compounds [18]. Graded pore structures are promising to reduce the flow resistance of the substrate that eventually can limit the flux of the asymmetric membrane structure [19,20], which can then be based on constant pore volume (fewer, but larger pores on one side of the structure), constant pore size (more pores of identical size on one side of the structure), or a combination of both. Utilizing traditional techniques, the ability to engineer pore structures is limited to manipulation of thermal fugitive particle orientation and sta-

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bility during the slurry process [20]. One negative aspect of this technique is that the porosity induced is usually randomly organized and non-optimized with an important tortuosity resulting in a detrimental increase of the pressure loss through the sample at high feed flow operations. This usually leads to concentration polarization resistance, i.e. the accumulation of retentated molecules (N_2, CO_2) and the depletion of the active molecule (O_2) hindering the permeation [21].

To overcome this drawback, emerging shaping techniques are the focus of ongoing studies for the fabrication of porous ceramic samples, presenting an organized porosity that could lead to a low tortuosity and a drastic decrease of pressure loss in comparison with conventional porous samples [21]. Among these techniques, freeze casting, also known as ice-templating, emerged to be a very promising alternative [22,23]. Indeed, it allows the fabrication of highly organized porous ceramic samples using most of the time water as pore former agent. Concretely, it consists of freezing generally the bottom of a ceramic slurry followed by the sublimation of the solvent by freeze-drying at both low pressure and temperature. The freezing of the ceramic slurry induces, in a repetitive pattern, the growing of vertical solvent crystals along the freezing direction and the associated rejection of ceramic particles between these crystals. Finally, the as-obtained green body after solvent removal by freeze-drying is sintered for consolidation and the final freeze-cast sample exhibits hierarchically vertically aligned porosity, which is the replica of the original solvent crystals. This is a very versatile technique, since every ceramic material can be freeze-casted and by modifying the powder characteristics, the freezing conditions or the slurry formulation, both porosity size and shape of the sample can be tailored for the targeted requirements. Up to now, such technique was mainly implemented for bone substitution [24,25], but the possibility to fabricate highly ordered ceramic samples has attracted the attention of the scientific community especially in the energy production field [17], where several systems are based on asymmetric ceramic membranes. The manufacture of asymmetric membranes based on mixed ionic-electronic conductor by freeze-casting started in the last years. Recently, the mechanical properties of freeze-cast materials have been reported by different research groups based on their pore structure. For example, Ojuva et al. [26] investigated the effect of solids loading and freezing temperature on zeolite materials and related the compressive strength to the pore aspect ratio. Seuba et al. [27–29] characterized the compressive behavior of freeze-cast ceramics in a broad porosity range from 45% to 80% and improved the honeycomb out-out-plane model by considering microstructural effects. However, these studies are mostly limited to compressive strength and in the membrane application relevant conditions the stress induced in a bending mode is more critical to stability the materials. However, work considering bending strengths and associated microstructural effects of unidirectional porous ceramics is still lacking.

Elastic modulus and fracture stresses along with a statistical analysis are a basis for a mechanical reliability assessment, being characterized for the current material. In terms of warranting production orientated mechanical reliability, proof testing has become one of the standard practices in many engineering applications, being a further aim of the current work. The typical reasoning for employing proof-testing is as follows. Within a population there may be specimens which are sufficiently weak that the function of the material and hence entire component is severely impaired. Proof-testing the population and hence entire batch of components will necessarily remove these weak specimens. Furthermore, there is a guaranteed minimum strength and related time to failure for the remaining components, which ensures the successful operation of the material beyond that value [30]. In proof testing, ceramic components are loaded to stresses greater than those expected in service in order to break the week components and thus truncate the lower end of the strength distribution. In this manner, weak components are eliminated before they can be placed in service. When the material is loaded thereafter in service, the failure process is assumed to result from flaws which require strengths or times to failure in excess of the proof-load conditions [31,32]. Some of the important applications for proof testing include the various uses of aerospace industry [33], electrical porcelain insulators [34], and optical fibers [35].

Hence, the current work is a systematic comparison of the mechanical properties for mainly freeze-cast ceramic 3YSZ samples of different porosities with a comparison to respective pressed/sintered material. For each batch of samples, elastic behavior and fracture stresses have been determined using ring-on-ring bending tests and statistically analyzed. In addition, a proof test is carried out for one particular batch. The obtained mechanical parameters are compared and concisely discussed considering microstructural analysis and also the results of complementary pressure drop experiments.

2. Materials and methods

Pressing/sintering and freeze-casting have been utilized as conventional and original ceramic shaping methods, respectively, based on 3 mol% Y_2O_3 doped ZrO_2 (3YSZ) powder. Details on materials preparation and testing are given in the following sections.

2.1. Freeze-cast 3YSZ

Freeze cast samples were fabricated as follows: The 3 mol% Y_2O_3 doped ZrO_2 (3YSZ) powder obtained from Tosoh was ball-milled in acetone during 48 h to ensure homogeneity and a final average particle size of about 2 μm. Porous monoliths were elaborated by ice-templating using the freeze-casting technique according to optimized samples fabricated in previous works [36,37]. Basically, a slurry containing the ceramic powder, water (30–40 wt%) as solvent, a polyacrylate-based dispersing agent (1–4 wt%), polyethylene glycol (1–4 wt%) (Sigma-Aldrich) and zirconium acetate complex (ZRA from Sigma-Aldrich, 24 gL^{-1}) as structuring agent if desired was stirred for 24 h to get a good particle distribution. In order to evaluate the influence of the porosity percentage over the mechanical properties, samples with different initial ceramic powder loading of 57, 60, 63, 66 and 70 wt% have been fabricated. The shaping process was as follows: the slurry was poured into a Teflon mold to get a sample of 1 cm height and cooled using copper rod cooled by liquid nitrogen. After complete freezing, the samples were removed from the mold and ice crystals were sublimated by freeze drying at −53 °C and reduced pressure during 24 h using a Scanvac commercial freeze-dryer. The samples were then sintered at 1390 °C under air during 6 h. Both heating and decreasing ramps were 2 K/min. To ensure that only the steady-state anisotropic structure was tested, disc-shape samples were cut out from the middle part of the cylinder samples, to exclude the denser top section as well as the isotropic and cellular zones. [38,39] The final diameter of the sample was 10 mm and the final thickness of 1 mm was adjusted by grinding the sample firstly by grinding papers from P#120 to P#1000 and then by a final cloth polishing in 5 μm, 2 μm and 1 μm diamond suspension. Debris is removed by acetone cleaning followed by ultrasonic cleaning and drying at 60 °C.

The influence of the presence of a dense top layer over the mechanical properties has also been studied. For this, a slurry made of an 8YSZ powder from Tosoh (previously ball milled during 24 h in acetone) and a binder (6 wt% ethylcellulose in terpineol) in a 50:50 wt ratio has been prepared and screen-printed over the porous