Ceramics International 42 (2016) 15177–15182

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Mechanical properties of tape casted Lanthanum Tungstate for membrane substrate application

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ARTICLE INFO

Article history:
Received 10 May 2016
Received in revised form
16 June 2016
Accepted 17 June 2016
Available online 17 June 2016

Keywords:
Ceramics
Membrane substrate
Porosity
Mechanical properties
Strength
Elastic modulus

ABSTRACT

Advances in the development of asymmetric membrane concepts require the development of porosity optimized, mechanically reliable substrate materials. The current study focuses on the characterization of the room temperature mechanical properties of tape casted Lanthanum Tungstate of different porosities for membrane substrate applications. Elastic modulus and hardness are assessed using indentation testing. Characteristic strength and Weibull modulus are determined from data obtained using a ball-on-3-balls test that is particularly advantageous for the rather thin tape casted material. Particular emphasis is placed on the effect of the surface composition onto the fracture strength.

1. Introduction

Ceramic materials exhibiting elevated temperature mixed proton–electron conductivity have attracted increasingly attention in the field of hydrogen based technologies [1–3]. Candidate membrane materials that combine appreciable conductivity with sufficient chemical, mechanical and (hydro-) thermal stability for operation at high temperatures can be used in Proton Conducting Solid Oxide Fuel Cells (PCFCs), in catalytic membrane reactors or for H_2 separation [4–6]. Similar as already verified for oxygen transport membranes, high permeation rates can be achieved by thin membrane layers [7] supported by a porous substrate. This makes the mechanical stability of the substrate an important aspect [8,9].

Recent developments led to a novel class of ceramic materials, the lanthanide tungstate compounds posing the general formula $Ln_xWO_{3+1.5x}$, with $x \approx 6$ ($Ln_6WO_{12-\delta}$) with ordered defective fluorite structure or disordered pyrochlore structure [10]. These structures, in particular Lanthanum tungstates (LaWO) with general formula $La_{28-x}W_{4+x}O_{54+\delta}v_{2-\delta}$ where $x=0.74\div1.08$ (La/W$=5.75\div5.3$) and $\delta=1.11\div1.62$ ($\delta=3x/2$) [11,12] exhibit sufficient elevated temperature electron-proton conductivity in hydrogen containing atmospheres [13,14] and acceptable stability in CO_2 containing atmospheres [15,16].

Advanced membrane designs are based on a thin layer supported by a porous substrate [17,18]. As stated by Wagner's theory [19], the H_2-transport through a bulk membrane depends not only on material-related properties (ambipolar conductivity) and operation-related parameters (temperature and pressure) but also on the thickness of the membrane. Thin membranes can be deposited on a porous substrate by advanced manufacturing methods. Moreover, to obtain high permeation rates through the supported membrane, along with reducing the membrane thickness down to certain critical thickness, where surface kinetic phenomena start to control the permeation process, the substrate needs to be also as thin as mechanically tolerable to minimize the concentration polarization limitations [20].

Ceramic membrane materials can exhibit complex mechanical behavior [21–26]. The mechanical reliability of the cell depends mainly on the porous substrate, where porosity is expected to influence the mechanical properties [27]. Moreover, due to the operation at high temperatures, thermal expansion mismatch (between the dense layer and the porous substrate) can result in significant residual stresses and bending or fracture of the layered structures [6,28,29]. Furthermore, the thermally-induced cation diffusion can lead to undesired grain boundary segregations and secondary phase formation [13], which may decrease the material/membrane performance and its integrity [23]. Thermal expansion

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http://dx.doi.org/10.1016/j.ceramint.2016.06.109
0272-8842/

coefficients of different membrane materials including LaWO and substrate material were compared in [30], while chemical compatibility data were reported in [31]. In order to minimize eventual interaction of component constituents and possible thermal mismatches between the substrate and membrane material, often the same material is used to manufacture a dense membrane and porous substrate [6,14,24]. For achieving sufficient gas flow toward the membrane layer, a macro-porous support should have a porosity of 30–40 vol% [6].

Planar membrane designs offer the benefit of large surface area as well as the ability to scale-up [19]. The most beneficial manufacturing method for ceramic membranes for planar designs is the tape casting, since it provides maximum flexibility in terms of sizing and mass production [32]. Tape casting is a well-established process for the fabrication of large-area ceramic sheets [33]. The typical thickness of the tape-cast components ranges between a few μm to about 1 mm depending on the tape-casting device. The main advantage of this technology is the high automation and its proximity to industrial-scale applications. Sequential tape casting originally invented in Jülich, has been already used for the fabrication of components for solid oxide fuel cells [34,35], as well as for oxygen separation membranes and modules [19,36,37], and is nowadays valid as a standard fabrication method.

The manufacturing of stable and defect-free supported LaWO membranes with an optimal architecture poses a serious challenge as addressed in [24] and studies on the performance of asymmetric LaWO membranes are limited. In fact, in [38] a H_2 permeation of 0.04 ml min^{-1} cm^{-2} at 900 °C was demonstrated in humid atmosphere (2.5 vol% H_2O, with 9.75% H_2) for an asymmetric membrane with a thickness of 25–30 μm with the same material substrate.

However, for an optimization of the substrate production, the effect of the substrate porosity on the resulting mechanical properties, elastic and fracture, needs to be assessed [7,8,20]. The quality of ceramic components is strongly influenced by the manufacturing process as shown in [24]. Influence factors are geometry and surface quality (e.g. contact damage, scratches) and microstructure (e.g. grain and flaw size distribution).

The structural integrity of brittle materials depends on their strength. If an applied external stress overcomes the fracture stress, spontaneous crack growth occurs, which may cause failure of the material. Therefore, fracture stresses and especially the strength obtained via statistical analysis is an important parameter to account for mechanical stability of membrane substrates and needs to be characterized. It is difficult to characterize the rather thin membrane substrates properly by standard biaxial tests that are widely applied for standard size specimens made of bulk and dense material. For example, ring-on-ring testing requires very flat surfaces as proper testing conditions [39]. Otherwise, measurement uncertainties can influence significantly the determined strength parameters, as demonstrated in [40].

An alternative is the ball-on-3-balls (B3B) biaxial bending test, which has proven to be an effective and reliable strength testing method of small ceramic components (i.e. specimens with a volume of less than 1 mm^3 have been successfully tested), [41–43]. It further tolerates slight specimen imperfections in the determination of strength (stress at the moment of failure) without biasing the testing accuracy. Other parameters such as misalignment, small deviations of the threefold geometry or some buckling and wrapping of the specimens have only little effect on the measured maximum fracture stress of the specimens [44].

The aim of the current study is to determine the mechanical properties of porous LWO substrate membrane materials manufactured by a tape casting technique via the B3B test, with special emphasis on the effect of porosity on elastic modulus, hardness and fracture strength.

2. Experimental

Commercially available LaWO54 powder manufactured by spray pyrolysis (CerPoTech AS, Norway) was used for the slurry preparation. In order to reduce its sintering activity to suitable level, powder was calcined at 1100 °C. Three batches of materials with different porosity were tape cast by varying the pore former (rice starch) amount in the slurry were tested. Samples were labeled LaWO54-P30, LaWO54-P32, LaWO54-P39, respectively, where CPT stays for CerPoTech, P for porosity followed by a number signifying the porosity in %. The average thickness was 330 μm in green state and ~260 μm after sintering. The materials were sintered at 1500 °C with 3 h dwell time and tested in the as-sintered condition (application relevant surface condition).

Rectangular plates with dimensions 3×4 mm^2 were cut from sintered discs with 20 mm diameter by diamond saw cutting. Table 1 summarizes the materials details for porous LaWO54 plates tested with B3B method at room temperature (RT).

X-Ray diffraction (XRD) patterns were obtained in the 2 theta range from 10° to 80° using D4 ENDEAVOR (Bruker AXS GmbH, Karlsruhe, Germany) diffractometer with CuKα radiation. Crystal structures were obtained with software HighScore Plus 3.0 (PANalytical B.V., Almelo, Netherlands) from the Inorganic Crystal Structure Database (ICSD PDF-2) (Release 2004). The TOPAS program (Bruker AXS GmbH, Karlsruhe, Germany) was used for the quantitative phase analysis and lattice parameter determination.

Microstructural analysis was performed using scanning electron microscopy (SEM, SUPRA 50VP and Merlin, both Zeiss, Germany) on samples polished with diamond paste down to 0.25 μm. Elemental analysis was carried out by energy-dispersive X-Ray spectroscopy (EDS, Inca, Oxford Inst.). For porosity analysis of sintered specimens, SEM images of cross-sections were recorded and analysed using the Analysis Pro® analysis software.

The elastic properties of the porous samples were determined with depth sensitive indentation using a Vickers micro-indentation device HC100 (Fischer, Windsor, USA) on grounded and subsequently polished cross-section surface specimens (20×0.2 mm^2) according to guidelines listed in ASTM C1327-08 [45], see also [46–48]. The used range of indentation loads was 50 mN to 1000 mN.

The biaxial tensile strength was determined by the B3B testing method. Details on the configuration as well as the evaluation procedure are explained in detail elsewhere [34,35,37]. The four balls used in the test had a radius of 1.189 mm giving a support radius of 1.373 mm. A pre-load of 0.2 N was applied. The loading rate was 13.8 N/min. The tests were performed under displacement control using a universal testing machine Micro-strain (Messphysik, Fürstenfeld, Austria). The corresponding stress rates were calculated from the load vs. time curves. Tests were conducted in ambient air (relative humidity $18.5 \pm 2\%$) at room temperature (22 °C). The biaxial strength was calculated for every rectangular specimen from the maximum tensile stress (σ_{max}) during loading according to [37]:

$$\sigma_{max} = f\frac{F}{t^2} \quad (1)$$

where F is the maximum force at failure, t is the plate thickness,

Table 1
Materials details.

	Pore former, (wt%)	Porosity, (%)	Specimens, N	Thickness, (mm)
LaWO54-P30	20	30 ± 1	27	0.248 ± 0.009
LaWO54-P32	25	32 ± 1	21	0.254 ± 0.003
LaWO54-P39	35	39 ± 1	13	0.239 ± 0.002