



Original Article

MgO as a non-pyrolyzable pore former in porous membrane supports

Haugen A.B.^{a,*}, Geffroy A.^{b,1}, Kaiser A.^a, Gil V.^{a,2}^a Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark^b Department of Materials, Polytech Nantes, Rue Christian Pauc CS 50609, 44306 Nantes Cedex 3, France

ARTICLE INFO

Keywords:

Oxygen transport membrane
Y-TZP
Porous ceramic
Thermoplastic shaping
Gas permeability

ABSTRACT

The gas permeability of $Y_{0.03}Zr_{0.97}O_2$ (3Y-TZP) porous supports from thermoplastic feedstocks has been improved by adding MgO as a *non-pyrolyzable* pore former. Common *pyrolyzable* pore formers such as graphite often produce tortuous and narrow pore channels with low gas permeability, limiting the performance of oxygen transport membranes or other membranes relying on gas transport to the active membrane surface. Thermoplastic feedstocks for extrusion of tubular 3Y-TZP supports were prepared with four different amounts of pyrolyzable pore formers and/or MgO as non-pyrolyzable pore former. The MgO was removed *after* sintering by leaching in acetic acid. With this technique we obtained porosities above 70 vol% and gas permeabilities above $3 \cdot 10^{-14} \text{ m}^2$. Compared to samples with only pyrolyzable pore formers, the non-pyrolyzable pore former increases the gas permeability and reduces the tortuosity.

1. Introduction

Porous ceramic supports are key components in asymmetric, inorganic membranes [1,2]. Oxygen transport membranes for example, only reach sufficiently high performance when used as thin, dense membranes supported on thicker, gas-permeable macroporous supports [3,4]. Their fabrication should be suitable for large volumes, also in non-planar shapes such as tubes [1,3]. One option is extrusion of thermoplastic feedstocks containing pore formers. Thermoplastic feedstocks provide high green body strength even for thin-walled (0.5–1 mm) structures, and although they require slow debinding, the drying of fragile tubes as in water-based extrusion can be avoided [5]. Porosity in the thin-walled support tubes can be produced from coarse starting powders or from pore formers. For the preparation of asymmetric membranes the latter is preferred, as it allows using finer ceramic powder with higher shrinkage during sintering, suitable for co-sintering of the support layer with a dense membrane layer [6,7].

The porous support's gas permeability (k , the Darcy gas permeability coefficient [8]) depends on the volume fraction of porosity (ϕ), the pore diameter (D_p) and the tortuosity factor (τ), and can be expressed as:

$$k = \frac{\phi D_p^2}{16\tau} \quad (1)$$

where the tortuosity factor takes the value 2 for the ideal case with

parallel pore channels (capillary permeability) [9]. Porous supports for oxygen transport membranes should have gas permeability in the range of 10^{-14} m^2 to avoid limitation in the gas supply to the membrane surface [4]. Eq. (1) then suggests for example a combination of pore channels wider than $1 \mu\text{m}$ and porosity above 40% as the targets for reaching 10^{-14} m^2 permeability (assuming a tortuosity factor of 2).

Pyrolyzable pore formers - such as graphite, starches and polymers - usually burn off or decompose at temperatures (400–700 °C) that are relatively low compared to the final sintering temperature (typically > 1200 °C). A consequence of this low-temperature removal is significant densification after the pores are formed, such that they get isolated and cannot contribute to gas permeation. Furthermore, spherical pore formers are often chosen to avoid shear forces aligning them perpendicular to the desired direction of gas flow. But this also makes the connected pore channel through the material more dependent on the contact area of the spherical pore former particles than the actual size of the pore former particles. Pyrolyzable pore formers therefore often give a pore structure with a high volume of large, spherical pores, but with narrow, tortuous channels that form bottlenecks between the pores [10]. Our previous work⁷ with the pyrolyzable pore formers PMMA and graphite in thermoplastic feedstocks for membrane support also showed this. Approximately 50 vol% of pore former within the dry content provided sufficient porosity (40%), but more than 60 vol% pore formers were required before the permittivity target (10^{-14} m^2) was reached, since the quite spherical pores were poorly connected and the

* Corresponding author.

E-mail address: ahua@dtu.dk (A.B. Haugen).¹ This work was performed during the author's internship at the Technical University of Denmark.² Present address: Fundación Agencia Aragonesa para la Investigación y Desarrollo (ARAID)-Tecnologías del Hidrógeno en Aragón, Spain.

pore size not efficiently enlarged by increasing the pore former content.⁷ The resulting high porosity (> 60%) limits the samples' mechanical strength. A way of improving pore connections, such that the pore size can be increased more efficiently at lower pore former content, is therefore desired.

A less studied alternative to pyrolyzable pore formers are *non-pyrolyzable* pore formers. One example is reduction of NiO to Ni in solid oxide fuel cell anode supports [11], such that porosity is generated after sintering from the volume decrease associated with the reduction. Additional porosity has also been created by leaching out the remaining Ni with acid [12,13]. Some studies of porosity from oxides leached with acid have also been reported: MgO from Ce_{0.8}Gd_{0.2}O [14], and ZnO from Y_{0.08}Zr_{0.92}O₂ [15].

In this work, we have investigated whether oxide leaching was compatible with thermoplastic feedstocks previously developed [7] for extrusion of Y_{0.03}Zr_{0.97}O₂ (3YSZ or 3Y-TZP) porous oxygen transport membrane supports, and to what extent the non-pyrolyzable pore formers could improve the gas permeability of the pore network generated by pyrolyzable pore formers. We chose MgO as the non-pyrolyzable pore former due to its low cost and toxicity, solubility in water, and high reactivity towards weak acids also as an oxide. We studied four feedstocks with different amounts of pyrolyzable pore formers and/or MgO as non-pyrolyzable pore former, sintered in the temperature range (1250–1400 °C) which is relevant for co-sintering of the 3Y-TZP supports with the thin layer of the oxygen transport membrane.

2. Experimental

2.1. Porous support processing

The composition of the thermoplastic feedstocks for porous 3Y-TZP supports are listed in Table 1. A test feedstock (Y-TZP-MgO-test) was first made to check the compatibility of MgO with the thermoplastic feedstocks previously developed [7] for only 3Y-TZP (Y-TZP-test). For these test feedstocks, the Y-TZP powder was TZ-3Y-E (d₅₀ = 0.04 μm, Tosoh, Japan) and the MgO powder Product #12R-0801 (Inframat, USA) calcined for 10 h at 1000 °C (d₅₀ = 0.15 μm). Based on the results from the test feedstocks, the ceramic powders for the further study were changed to TZ-3YS-E (d₅₀ = 0.09 μm, Tosoh, Japan) and MgO from MC10-200 (Martin Marietta Magnesia Specialties LLC, USA) milled to d₅₀ = 1.8 μm. Stearic acid (Sigma-Aldrich, USA) was used as a surfactant, in an amount equivalent to 1.5 monolayer coverage of all 3Y-TZP and MgO [16,17]. The pyrolyzable pore formers were graphite (d₅₀ = 18 μm, FormulaBT SLA1518, Superior Graphite, USA) and PMMA (d₅₀ = 9 μm, MR-10G, Esprix, USA), in the volume ratio 2:1. The above mentioned chemicals constituted the dry content, which together made up 65 vol% of the feedstocks. The remaining 35 vol% were the thermoplastic binders ethylene-vinyl acetate copolymer (Elvax® 250, DuPont, USA) and paraffin wax (melting point 53–57 °C, Sigma-Aldrich, USA), in the volume ratio 2:1.

Thermoplastic feedstocks with a total volume of 55 ml were mixed and compounded at 110–115 °C (Kneader 50N, Brabender, Germany).

Table 1

Composition of the thermoplastic feedstocks for studying MgO as non-pyrolyzable pore former. The vol% refer to the composition within the solid content.

Feedstock code	Vol% MgO as pore former	Vol% pyrolyzable pore formers	Vol% 3Y-TZP	Total vol% pore formers
Y-TZP-test/ 0m-62p-38z	0	62	38	62
Y-TZP-MgO-test/ 13m-62p-25z	13	62	25	75
20m-38p-42z	20	38	42	58
33m-0p-67z	33	0	67	33

Discs of 24 mm diameter and 1–2 mm thickness were shaped by warm pressing and cutting at 100 °C. The samples were debinded in air with a slow heating rate (10 °C/h) and with isothermal holds (2 h) at 250, 400 and 650 °C or 200, 300, 350 and 650 °C (no difference observed), then ramped with 30 °C/h to the sintering temperature (1250–1400 °C, 2 h) and finally cooled at 100 °C/h to room temperature.

Leaching in acetic acid (Sigma Aldrich, USA) and distilled water was studied with the Y-TZP-MgO-test feedstock sintered at 1300 °C. Acid strength, volume and temperature was varied, and the time for complete leaching observed. Complete leaching was defined as removal of the mass of MgO added to the sample minus the MgO that dissolves in the 3Y-TZP structure [18] and therefore cannot be (as easily) leached out. Based on this leaching study, the chosen procedure for further work was to soak the samples in 33 ml 60% acetic acid per g sample until complete leaching was obtained. This procedure required 30 h for samples of feedstock Y-TZP-MgO-test and 13m-62p-25z, while for 20m-38p-42z the required leaching time was dependent on the sintering temperature: 30 h + 70 h for 1250 °C-samples, 30 + 120 h for 1300 °C-samples, and 120 + 120 h for 1400 °C-samples. For samples from feedstock 33m-0p-67z, 30 h of the conventional 60% acetic acid at room temperature was followed by 70 h in 37% hydrochloric acid (VWR Chemicals, USA) and 300 h in 100% acetic acid at 50 °C. The samples were rinsed in distilled water and dried between each leaching step.

The samples are named according to the scheme: “vol% MgO” – “vol% pyrolyzable pore formers” – “vol% 3Y-TZP” – “sintering temperature (in °C)” – “leaching state (L for leached, UL for un-leached)”. For example, 13m-62p-25z-1300-UL contains 13% MgO, 62% pyrolyzable pore formers (graphite and PMMA) and 25 vol% 3Y-TZP within the solid content, has been sintered at 1300 °C, and has not been leached.

2.2. Characterization

Debinding, densification and phase composition were studied with thermogravimetry (STA 409PC/PG, Netzsch, Germany), dilatometry (DIL 402, Netzsch, Germany) and x-ray diffraction (D8, Bruker, USA). Mercury porosimetry (Poremaster® GT, Quantachrome Instruments, USA) was used to measure open porosity and pore size distribution of sintered samples. The microstructure of polished sample cross-sections was studied by SEM (TM 3000, Hitachi, Japan) and EDS (SDD, Bruker, USA). The flow of N₂ through the samples under a pressure gradient of 200 kPa at room temperature was used to measure the Darcy gas permeability coefficient, *k* [8].

3. Results and discussion

3.1. Effect of MgO on the thermoplastic feedstock

MgO could be included in the thermoplastic test feedstock (Y-TZP-MgO-test) without any challenges during the mixing and kneading. By thermogravimetry (Fig. 1a), we can also see that MgO does not significantly change the debinding behavior; in both feedstocks with and without MgO we observe weight loss at low temperature (200–450 °C) from polymers (stearic acid, Elvax and PMMA) and at higher temperature (600–800 °C) from the graphite. Still, almost all of the samples from Y-TZP-MgO-test contained small blisters on their surfaces after sintering. Slightly adjusting the temperature of the isothermal holds during debinding did not have any effect. Inhomogeneous distribution within the feedstock and local high polymer content was therefore a probable cause of the blisters, and the ceramic powder size was increased to improve the feedstock homogeneity in the further studies.

MgO had a pronounced effect on the dilatometry curve of the feedstock (Fig. 1b). When adding MgO, the densification onset shifts from about 1000 to 900 °C, and the shrinkage rate shows two peaks, at about 1100 °C and at about 1275 °C. This shows that MgO lowers the sintering temperature of the feedstock, in accordance with the lower

Download English Version:

<https://daneshyari.com/en/article/7898233>

Download Persian Version:

<https://daneshyari.com/article/7898233>

[Daneshyari.com](https://daneshyari.com)