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Published in:
Journal of the European Ceramic Society

Link to article, DOI:
[10.1016/j.jeurceramsoc.2018.02.039](https://doi.org/10.1016/j.jeurceramsoc.2018.02.039)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Haugen, A. B., Geffroy, A., Kaiser, A., & Gil, V. (2018). MgO as a non-pyrolyzable pore former in porous membrane supports. *Journal of the European Ceramic Society*, 38(9), 3279-3285.
<https://doi.org/10.1016/j.jeurceramsoc.2018.02.039>

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

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** This work was performed during the author's internship at the Technical University of Denmark

*** Currently at: Fundación Agencia Aragonesa para la Investigación y Desarrollo (ARAID)-Tecnologías del Hidrógeno en Aragón, Spain

Abstract

The gas permeability of $\text{Y}_{0.03}\text{Zr}_{0.97}\text{O}_2$ (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.

Graphical abstract

Keywords: Oxygen transport membrane; Y-TZP; porous ceramic; thermoplastic shaping; gas permeability

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 coefficient⁸) 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 Eqn. 1 then suggests for example a combination of pore channels wider than $1 \text{ }\mu\text{m}$ 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 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 $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}$,¹⁴ and ZnO from $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_2$.¹⁵

In this work, we have investigated whether oxide leaching was compatible with thermoplastic feedstocks previously developed⁷ for extrusion of $\text{Y}_{0.03}\text{Zr}_{0.97}\text{O}_2$ (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 developed⁷ for only 3Y-TZP (Y-TZP-test). For these test feedstocks, the Y-TZP powder was TZ-3Y-E ($d_{50} = 0.04 \mu\text{m}$, Tosoh, Japan) and the MgO powder Product #12R-0801 (Inframat, USA) calcined for 10 h at 1000 °C ($d_{50} = 0.15 \mu\text{m}$). Based on the results from the test feedstocks, the ceramic powders for the further study were changed to TZ-3YS-E ($d_{50} = 0.09 \mu\text{m}$, Tosoh, Japan) and MgO from MC10-200 (Martin Marietta Magnesia Specialties LCC, USA) milled to $d_{50} = 1.8 \mu\text{m}$. 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 ($d_{50} = 18 \mu\text{m}$, FormulaBT SLA1518, Superior Graphite, USA) and PMMA ($d_{50} = 9 \mu\text{m}$, 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.

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

Thermoplastic feedstocks with a total volume of 55 ml were mixed and compounded at 110-115 °C (Kneader 50N, Brabender, Germany). 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 structure¹⁸ 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 unleached)”. 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 (Figure 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 (Figure 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 sintering temperature of MgO compared to 3Y-TZP.¹⁹

Figure 1. a) Thermogravimetric analysis (TGA), and b) dilatometry of test feedstocks for porous 3Y-TZP supports with MgO as a non-pyrolyzable pore former. [1 column width]

Leaching studies on Y-TZP-MgO-test sintered at 1300 °C showed that acetic acid is a suitable leaching agent. Complete leaching was observed after removal of 86 wt% of the MgO. Using 133 ml acid per gram sample lead to complete leaching after 10-30 h with 60 % acetic acid (Figure 2a). For short leaching times, and especially for high concentration of acetic acid, the completeness of leaching is negative, meaning that the sample gained weight during the leaching. This can be explained by formation of solid magnesium acetate. This acetate can be removed by soaking in water, but the shorter the leaching time, the more challenging is the removal from inside the porous network. Figure 2b) shows that the amount of acid could be reduced to 33 ml/g without affecting the completeness of leaching after 30 h. Finally, Figure 2c) shows that increasing the temperature reduces the time required for complete leaching; at 50 °C with 133 ml/g it only takes 2 hours to complete the leaching. This is similar to observations by Wang et al.¹⁴ on leaching of MgO from Ce_{0.8}Gd_{0.2}O₂. Based on the leaching study, all further leaching was performed with 33 ml of 60 % acid per sample. Since complete leaching was observed after 30 h without heating, the leaching was performed at room temperature in order to simplify the setup. Using 25 % rather than 60 % might

be advantageous for a large-scale leaching of porous supports, since it lowers the hazard classification of the acid from “corrosive” to “irritant”. Leaching in water did not result in any measurable weight loss, not even using hot water (up to 100 °C) combined with very long time (up to 200 h).

Figure 2. Leaching of MgO from 3Y-TZP using acetic acid in a) different concentrations (at room temperature, 133 ml/g) b) different amounts (60 %, room temperature) and c) different temperatures (60%, 133 ml/g). [Full page width]

XRD on sintered samples (Figure 3) shows that MgO affects the crystallographic structure of the 3Y-TZP porous supports. All samples have a polymorph of zirconia as their main phase. Before leaching, MgO is present as a separate phase in the Y-TZP-MgO samples, but this MgO phase is completely removed by the leaching. Still, in Y-TZP-MgO-test-1250-L there are extra peaks compared to Y-TZP-test-1250 at either side of the main reflection at $2\theta = 30^\circ$. These peaks can be indexed to monoclinic zirconia. Upon increasing sintering temperature the Y-TZP-test samples remain unaffected while the structure of the Y-TZP-MgO-test samples changes: the zirconia reflections (e.g. at $2\theta = 30^\circ, 35^\circ, 51^\circ, 60^\circ$ and 75°) transform from doublets to singlets, indicating a transition from monoclinic and tetragonal to cubic zirconia.

3Y-TZP is used as the membrane support in this work since it offers high toughness as well as chemical and thermal compatibility with many oxygen transport membrane materials. This toughness originates from a transition from monoclinic to a metastable tetragonal phase, which is maximized at 3 mol% Y doping in zirconia.²⁰ It is known that also Mg, up to 15-20 mol%, can dissolve in the zirconia structure.¹⁸ The 14 wt% non-leachable MgO in our work corresponds to 13 mol% of MgO forming a solid solution with Y-TZP, hence in good correlation with the previous reports.¹⁸ Mg can stabilize the tetragonal phase in zirconia,²⁰ but Mg in Y-doped zirconia can

promote a cubic phase instead.²¹ This is also what we observed here, with the change from tetragonal to monoclinic and cubic phases when MgO is introduced. Monoclinic and cubic phases of zirconia with 3 mol% Y have lower toughness than 3Y-TZP,²⁰ hence our approach with MgO as the non-pyrolyzable pore former will lower the toughness of the porous supports. On the other hand, at a given sintering temperature the matrix structure of 3Y-TZP doped with MgO densifies more than undoped 3Y-TZP (Figure 1b), and its higher density could counteract its intrinsic lower toughness. The aim of this work was to check the compatibility of non-pyrolyzable pore formers in the thermoplastic feedstocks and their effect on the pore structure and the gas permeability, but further development of 3Y-TZP porous supports with MgO as the non-pyrolyzable pore former should include a thorough investigation of mechanical properties. Alternatively, MgO could be added to zirconia to instead of to 3Y-TZP, which upon meticulous control of processing temperature and grain size can provide Mg-stabilized zirconia.^{20, 21}

Figure 3. XRD patterns of 3Y-TZP porous supports with MgO as non-pyrolyzable pore former. The reflections from MgO are assigned according to PDF card 89-7746. All other peaks are tetragonal (48-0224), monoclinic (37-1484) or cubic (30-1468) zirconia. [1 column width]

3.2 Microstructure of 3Y-TZP porous supports with MgO as pore former

After the initial test feedstocks, four feedstocks with varying amounts of MgO and pyrolyzable pore formers were made (compositions in Table 1). Properties of all these samples are listed in Table A.1.

All thermoplastic feedstocks could be kneaded into a homogenous feedstock and sintered into defect-free samples. This demonstrates both that 35 vol% polymers was suitable for shaping all compositions, and that changing to coarser 3Y-TZP and MgO powders improved the feedstock homogeneity (compared to the test feedstocks) such that blisters were avoided. The total linear shrinkage during sintering increased slightly with addition of MgO, but was mostly affected by the sintering temperature and the amount of pyrolyzable pore former (Table A.1).

Figure 4 shows SEM micrographs after sintering at 1300 °C, before and after leaching. MgO are the dark grey spots and pores from the pyrolyzable pore formers are black. The sample without MgO (0m-62p-38z-1300, Figure 4a) contains large pores (5-20 µm) from the pyrolyzable pore formers, and small pores (<1 µm) between the grains within the 3Y-TZP matrix. When MgO is introduced (Figures 4b-d), the smaller pores disappear and the matrix phase appears denser, while the size and shape of pores from pyrolyzable pore formers seem to be unaffected. MgO is present as evenly distributed 1-5 µm particles, as expected from their particle size ($d_{50} = 1.8 \mu\text{m}$). The shape and size distribution of MgO can be clearly seen in sample 33m-0p-67z-UL (Figure 4d), since this sample does not have pyrolyzable pore formers. Complete leaching was obtained in 13m-62p-25z and 20m-38p-42z, which is reflected in the lack of MgO after leaching (Figure 4e-f). In 33m-0p-67z (Figure 4g) on the other hand, there is no visible change in the MgO distribution and amount; only 0.12, 0.02 and 0.01 in completeness of leaching was obtained at 1250, 1300 and 1400 °C, respectively (Table A.1). The 3Y-TZP matrix phase remains intact during the leaching.

Figure 4. Microstructural change of 3Y-TZP porous supports with increasing content of MgO as non-pyrolyzable pore former (sintering temperature 1300 °C), before (top) and after (bottom) leaching. [1.5 column width]

EDS maps (Figure 5) show more clearly how the leaching affects the distribution of MgO and porosity. Like in Figure 4, the large MgO particles in 13m-62p-25z and 20m-38p-42z are

completely removed after leaching (Figure 5d-e), but with about 4 at% Mg left randomly distributed within the 3Y-TZP matrix (Table A.1). These 4% corresponds to the 14 wt% of the MgO that could not be leached out (Section 3.1). The EDS map for 33m-0p-67z after leaching (Figure 5f) is taken close to the surface of the sample (at the top in the picture). Here, we can clearly see that only the outer few micrometers have been leached. Similar maps of 33m-0p-67z sintered at 1250 °C show a leaching depth of ~20 µm, while after sintering at 1400 °C only MgO particles directly at the surface were leached out. Furthermore, the amount of Mg observed by EDS after leaching is 2-4 at% Mg in 13m-62p-25z and 20m-38p-42z, while it remains at ~20 at% in 33m-0p-67z (Table A.1). This indicates challenges in leaching samples with no or low pre-existing porosity, where the leaching depends on the acid “digging” its way into the sample through narrow channels. The work on 33m-0p-67z was therefore discontinued. Still, this knowledge is useful if the supports are to be co-sintered with e.g. oxygen transport membrane layers. The membrane must then be acid-resistant (e.g. based on Y-TZP or $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$), or the leaching must be performed on a pre-sintered, bare support *before* application and sintering of the membrane layer. Given how dependent the acetic acid penetration depth is on the support’s porosity (33m-0p-67z), carefully adjusted leaching parameters could also allow e.g. leaching only the inside of tubular supports while a membrane layer on the outside remains undamaged.

Figure 5. EDS maps visualizing the distribution of Mg (green), Zr (red) and pores (black) in 3Y-TZP supports (sintering temperature 1300 °C) with increasing amount of MgO non-pyrolyzable pore former. The top row samples are before and bottom row after leaching. [1.5 column width]

3.3 Porosity and pore size of 3Y-TZP porous support with MgO as pore former

Open porosity (vol%) and mean pore size (pore channel bottleneck) was measured with mercury porosimetry to quantify the effect of adding MgO as a pore former to the 3Y-TZP supports. The

porosity increases markedly upon leaching for all samples, and above 70 vol% is reached in 13m-62p-25z after leaching (Figure 6a). The measured open porosity is generally in close correlation with the porosity expected from the amount of pore formers (Table 1). The porosity values also show that MgO densifies the Y-TZP supports. For example, 13m-62p-25z has ~10 % lower porosity before leaching than 0m-62p-38z, although they both have the same amount of non-leachable pore formers. The mean pore size (Figure 6b) also increases with leaching, and the largest mean pore size (1.6 μm) is again found in 13m-62p-25z. Higher sintering temperature causes the porosity to slightly decrease and the pore size to slightly increase. The same trend was previously observed with thermoplastic feedstocks,⁷ and is related to the higher densification of the 3Y-TZP matrix, which both removes the small pores within the Y-TZP matrix and widens the pore channels.

Figure 7 reveals the effect of MgO as a non-pyrolyzable pore former on the cumulative pore volume distributions. Leaching of MgO increases the volume of large pore channels (2-10 μm) relative to the volume of very small pore channels (0.2-1 μm), while the median pore size remains less affected (Figure 7a). With increased sintering temperatures the entire pore size distribution shifts towards higher values (Figure 7b). Remarkably, the accumulated pore volume of 2-10 μm sized pores is increased from about 2.5 % at a sintering temperature of 1250 $^{\circ}\text{C}$ to about 25 % at 1400 $^{\circ}\text{C}$.

Figure 6. Open porosity (vol%) (a) and mean pore size (d_{50}) (b) vs. sintering temperature in the 3Y-TZP porous supports made with MgO as a non-pyrolyzable pore former. The legends apply to both plots. [1 column width]

Figure 7. Effect of MgO as non-pyrolizable pore former on cumulative pore volume of 3Y-TZP porous supports (a), and effect of sintering temperature (b). [1 column width]

3.4 Gas permeability of 3Y-TZP porous supports with MgO as pore former

Figure 8 shows how MgO as a non-pyrolizable pore former affects the gas permeability of the porous 3Y-TZP supports. Leaching increases the gas permeability in all samples, and with the highest amount of pyrolizable and non-pyrolizable pore formers (13m-62p-25z), the permeability after leaching is above $3 \cdot 10^{-14} \text{ m}^2$. This is almost twice as high as the corresponding sample (0m-62p-38z) without pyrolizable pore formers. The lower permeability of 13m-62p-25z-UL compared to 0m-62p-38z is as expected from the higher sintering and thereby lower porosity of the 3Y-TZP supports upon addition of MgO. When the amount of MgO as pore former is increased, but the total amount of pyrolizable pore formers is reduced (20m-38p-42z) the gas permeability also decreases,

but is still around $1 \cdot 10^{-14} \text{ m}^2$ after leaching. Finally, we can also see that the gas permeabilities of leached samples are relatively unaffected by the sintering temperature within the studied range (1250-1400 °C).

To assess the effect of the non-pyrolyzable pore formers, we should also consider their tortuosity. Eqn. 1 makes it possible to estimate the tortuosity factor based on the measured permeability, porosity and mean pore size. Figure 9 shows the calculated tortuosity factor for all samples. As expected, the leached samples have a lower tortuosity than the unleached, but we can also see a trend of lower tortuosity with increasing content of non-pyrolyzable pore formers. The latter is not only an effect of a higher total content of pore formers and a higher porosity, since this is lower in the samples with 20 % MgO (20m-38p-42z) than the other compositions. The low tortuosity factors demonstrate that the leached samples with MgO as non-pyrolyzable pore former are significantly closer to having cylindrical, straight pores (described by a tortuosity factor of 2), compared to both the unleached samples and the samples without MgO. This again indicates that we have succeeded in improving the pore connectivity as we aimed for.

Figure 8. Gas permeability of the 3Y-TZP porous supports before and after leaching. [1 column width]

Figure 9. The calculated tortuosity factor (from Eqn. 1) for the samples as a function of content of MgO as non-pyrolyzable pore former for different sintering temperatures before and after leaching. [1 column width]

4 Summary

Thermoplastic feedstocks for extrusion of porous $Y_{0.03}Zr_{0.97}O_2$ have successfully been prepared with MgO as a non-pyrolyzable pore former. The thermoplastic feedstocks were prepared with four different amounts of pyrolyzable pore formers (graphite and PMMA) and/or MgO. The MgO was removed *after* sintering by leaching in acetic acid to produce additional pores and enlarge pore channels. In fact, MgO as a non-pyrolyzable pore former in combination with the pyrolyzable pore formers resulted in widening of pore channels, porosities above 70 vol% and gas permeability almost twice as high as gas permeability obtained with only pyrolyzable pore formers. The achieved permeabilities of more than $3 \cdot 10^{-14} \text{ m}^2$ is three times higher than the required permeability for porous supports for oxygen transport membranes. Non-pyrolyzable pore formers decrease the tortuosity of the porous supports, which indicates that we have been successful in increasing the connectivity between the pores from the pyrolyzable pore formers. Leaching was only feasible in samples with pre-existing porosity from pyrolyzable pore formers, using MgO as the only pore former was therefore not successful. MgO accelerated the densification of the 3Y-TZP supports. MgO also partly dissolved in 3Y-TZP, such that the structure transformed from the high-toughness tetragonal phase to monoclinic and cubic phases. In conclusions, the advantages of achieving higher permeability with non-pyrolyzable pore formers should be weighed against the extra process step (leaching) and the expected lower toughness of Mg-Y-TZP compared to the use of partly stabilized

3Y-TZP as support material for oxygen transport membranes. Still, this work also opens up for non-pyrolyzable pore formers other than MgO, or supports other than 3Y-TZP within the same framework of thermoplastic feedstocks.

Acknowledgements

We thank Pernille Hedemark Nielsen and Jeanette Krambech for assisting with sample preparation for SEM and mercury porosimetry. Parts of the work has been funded by Energinet.dk through grant number 12403 “Highly Flexible Energy Production by Oxy-Fired Biomass Gasification”.

Appendix A

Table A.1. Results from all samples: Linear shrinkage during sintering, open porosity (ϕ), pore size (d_{10} , d_{50} and d_{90}), gas permeability coefficient (k), tortuosity factor calculated from Eqn. 1 (τ), and amount of Mg measured by EDS.

Sample name	Shrinkage (%)	ϕ (%)	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	k (m^2)	τ (-)	Mg (at%)
0m-62p-38z-1250	16	68	1.75	1.23	0.27	1.90E-14	3.7	
0m-62p-38z-1300	20	67	1.79	1.33	0.36	1.80E-14	4.8	
0m-62p-38z-1400	25	46	1.9	1.54	0.73	1.80E-14	3.8	
13m-62p-25z-1250-UL	17	56	1.34	1.03	0.41	1.1E-14	3.7	24
13m-62p-25z-1300-UL	21	53	1.63	1.27	0.50	9.6E-15	6.1	19
13m-62p-25z-1400-UL	25	38	1.77	1.43	0.69	7.2E-15	6.7	20
13m-62p-25z-1250-L	17	74	1.45	1.08	0.53	3.2E-14	1.7	2
13m-62p-25z-1300-L	21	74	13.4	1.40	0.67	3.4E-14	2.8	3
13m-62p-25z-1400-L	25	73	7.12	1.61	0.79	3.2E-14	3.8	4
20m-38p-42z-1250-UL	14	35	0.70	0.54	0.27	1.9E-15	3.4	23
20m-38p-42z-1300-UL	18	29	0.83	0.63	0.33	7.4E-16	9.7	26
20m-38p-42z-1400-UL	20	23	0.89	0.67	0.34	3.5E-16	18.7	23
20m-38p-42z-1250-L	14	62	0.96	0.67	0.39	9.8E-15	2.1	2
20m-38p-42z-1300-L	18	48	1.04	0.82	0.46	9.0E-15	2.3	4
20m-38p-42z-1400-L	20	44	1.22	0.96	0.48	8.9E-15	2.8	4
33m-0p-67z-1250-UL	14	14*						22
33m-0p-67z-1300-UL	15	7*						23
33m-0p-67z-1400-UL	15	5*						22
33m-0p-67z-1250-L	14	16*						22
33m-0p-67z-1300-L	15	7*						22
33m-0p-67z-1400-L	15	5*						22

* weight and dimensions (rather than mercury porosimetry) are used to estimate porosity

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