Porous control in silicon nitride-based support materials toward enhanced gas permeability

Thomas Konegger | Thomas Prochaska | Dominik Brouczek

Institute of Chemical Technologies and Analytics, Vienna, Austria

Correspondence
Thomas Konegger, TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-CT, 1060 Vienna, Austria. Email: thomas.konegger@tuwien.ac.at

Funding information
Austrian Science Fund, Grant/Award Number: P 29058

Abstract
Porous Si₃N₄ materials in tubular geometry are prepared by slip casting before partial sintering. A variety of material- and process-specific variables and their respective effects on densification and resulting pore morphology are systematically evaluated, focusing on starting powder type, amount of sintering additives, and sintering parameters including temperature and time. An increased β-Si₃N₄ content in the starting powder was found to promote the formation of a network of elongated grains exhibiting increased pore diameters, as opposed to a more finely featured pore network obtained from starting materials consisting of α-Si₃N₄. Following an iterative evaluation of processing variables, materials exhibiting a characteristic diametral compression strength (C-ring test) of 163 MPa and a Darcian permeability of $4.7 \times 10^{-15}$ m² at a total porosity of 41% were obtained, corresponding to an increase of over 40% in strength and of over 600% in permeability in comparison to materials obtained by α-Si₃N₄ powders at comparable porosities. These results demonstrate that the composition of Si₃N₄ powders significantly affects the resulting pore structure, and by combining the respective selection of starting materials with finely tuned sintering parameters, materials with superior performance in terms of mechanical properties as well as permeability characteristics are accessible.

KEYWORDS
gas permeability, mechanical properties, partial sintering, porous materials, silicon nitride

1 | INTRODUCTION

By combining excellent high-temperature properties, chemical resistance, and mechanical strength with controlled pore structures, porous ceramics have been established in numerous, highly diverse industrial fields, examples including catalyst carriers in chemical synthesis, metal melt filters in metallurgy, porous burners in industrial drying processes, or scaffolds for bone tissue engineering in biomedicine.¹,² One particular field of interest are porous ceramics as support structures for separation and catalysis applications, where high chemical, thermal, and mechanical resistance in combination with suitable flow characteristics for the permeation of liquid or gaseous media are required.

Silicon nitride (Si₃N₄) has gained high relevancy as a non-oxide ceramic material suitable for applications under high thermal and mechanical load by combining excellent high temperature properties, low density, and highly beneficial mechanical properties, which are a direct result of a well-tailorable microstructure.³ Examples for the application of Si₃N₄ include...
Numerous pathways have been explored to generate porous Si$_3$N$_4$ and related materials with tailored pore structures, including the addition and selective removal of pore-forming agents, combustion synthesis, solidification templating (i.e., freeze casting), phase separation, or direct foaming.

Partial sintering has been found to allow for a combination of excellent mechanical properties with a high degree of tailoring of the resulting pore structure. Here, the sintering process is stopped before full densification, thus providing a network of open pores between partly sintered ceramic particulates. One advantage in particular is the straightforward control of the resulting pore network by variation of well-adjustable process parameters such as sintering temperature or sintering time. Furthermore, specimens can be fabricated by conventional shaping processes such as slip casting.

Irrespective of aiming toward either a partial or a fully sintered state, several general aspects have to be considered during sintering of Si$_3$N$_4$. First, in order to avoid oxidation, sintering of Si$_3$N$_4$ is typically conducted in N$_2$ atmosphere. Second, in N$_2$ at ambient pressure, Si$_3$N$_4$ decomposes into elemental Si and N$_2$ at 1877°C, which sets a natural limit for maximum sintering temperatures. However, as the sintering rate of pure Si$_3$N$_4$ is insufficient below this temperature, sintering aids such as Y$_2$O$_3$ and Al$_2$O$_3$ are typically added in order to facilitate liquid-phase sintering. Furthermore, oxygen impurities present within the starting powder may lead to the additional presence of SiO$_2$, which also affects the densification behavior. In order to obtain fully dense Si$_3$N$_4$ ceramics, rather high sintering aid contents are oftentimes required (up to 20 wt%). For the preparation of porous Si$_3$N$_4$ ceramics, on the other hand, decreased sintering additive contents have been considered beneficial.

A third aspect to be considered involves the transformation of α-Si$_3$N$_4$ into β-Si$_3$N$_4$, occurring by dissolution of α-Si$_3$N$_4$ in the liquid phase and by re-precipitation as β-Si$_3$N$_4$. The transformation can be accompanied by profound microstructural changes due to the tendency of β-Si$_3$N$_4$ to form rod-like elongated grains, a consequence of the hexagonal crystal structure of the β modification. Transformation starts at 1550°C and plays a major part in the densification. With advancing transformation from α- to β-Si$_3$N$_4$, the densification rate decreases at 1650°C.

The degree of transformation in a material and, thus, its microstructural morphology, is not only determined by temperature and time, but also by the initial composition. Topates et al. demonstrated the importance of the $\alpha/\beta$ ratio in Si$_3$N$_4$ for the resulting microstructure in porous and densified Si$_3$N$_4$ by comparing two starting powders, one with an α-Si$_3$N$_4$ content of 80% and one with a β-Si$_3$N$_4$ content of 90%, both sintered at 1750°C and using CaCO$_3$ as sintering aid. Two reasons for the differences in resulting morphology were mentioned: the “location of precipitation” and the “grain impingement effect.” In the first case, re-precipitation of β-Si$_3$N$_4$ from the liquid phase can either occur on newly formed β-nucleii (predominant in starting powders containing high α-contents) resulting in more anisotropic features, or on pre-existing β-grains (predominant in starting powders containing high β-contents), resulting in a coarser, more equiaxed microstructure. In contrast, the grain impingement effect refers to the impact of the starting amount of β-Si$_3$N$_4$, where, in case of higher β-contents, the interparticle distance decreases, resulting in an equiaxed morphology due to impingement of grains. Owing to these differences in resulting pore morphology, in particular an increase in pore channel size in the presence of coarser, equiaxed grains, higher relative permeabilities were reported by the authors for powders with a higher initial β-Si$_3$N$_4$ content.

The majority of reports on the shaping of porous Si$_3$N$_4$ materials have been focused on relatively simple geometries, involving pressing or casting techniques. However, a tubular geometry, which can also be obtained in a straightforward manner by casting processes, is generally preferred for prospective applications as support material by facilitating an increased surface-to-volume ratio compared to planar configurations. In a previous publication, we reported on the methodological development of a slip-casting procedure suitable for the preparation of hollow-tube shaped porous Si$_3$N$_4$, achieving permeability values of up to $9 \cdot 10^{-16}$ m$^2$ at porosities in the range between 32 and 41%.

In this work, we aim toward elucidating the effects of a variety of material- and processing-inherent characteristics on the resulting pore morphology and, subsequently, mechanical and permeability properties, both in isolation of and in combination with each other. From a materials perspective, our overall objective is to significantly enhance the gas permeability while preserving or even enhancing the characteristic strength of porous tubular structures generated, thus providing guidelines for generating tailored non-oxide ceramic materials suitable as supports in separation and catalysis applications.

In particular, we focus on evaluating the effect of the starting powder type, in particular with respect to the α- and β-Si$_3$N$_4$ contents, the addition and quantity of sintering aids in the starting mixture, as well as typical sintering parameters such as temperature and time on the evolution and resulting morphology of porosity and, consecutively, its corresponding effect on mechanical and permeability performance.
size, particle morphology, and crystalline phase composition (Table 1; SEM images of starting powders are shown as Figure S1 in the Supplementary Information). As sintering aids, Al₂O₃ (CT3000SG, Almatis, Germany) and Y₂O₃ (Grade C, HC Starck, Germany) were used in varying amounts between 0.2 wt% and 2.5 wt% each, calculated with respect to Si₃N₄. As per the material datasheets, the powders contain up to 1.3 wt% of oxygen impurities (also shown in Table 1). Consequently, SiO₂ has to be taken into account as an additional sintering additive present in the starting mixture.

For slip casting, an aqueous slurry (solid loading: 36 vol%) containing Si₃N₄, deionized water, sintering aids, and an amino alcohol-based dispersant (Dolapix A88, Zschimmer und Schwarz, Germany; 1 wt% with respect to Si₃N₄) was prepared by ball milling for 24 h, using Si₃N₄ balls. The slurry was degassed using a planetary centrifugal mixer (ARE 250, Thinky Corporation, Japan) and cast into two-part plaster molds which had been prepared using a hemihydrate plaster (Supraduro), and which had been pre-dried at 50°C. The residency time in the molds was 70 s before the excess slurry was discarded. The cast specimens were dried in the mold at ambient conditions overnight before they were demolded and dried at 110°C for another 12 h. The dried greenbodies had a typical length of 60 mm, an outer diameter of 12 mm, and a wall thickness between 2 and 3 mm.

The samples were embedded in a powder bed consisting of equal parts of Si₃N₄ and BN powder and were sintered at ambient pressure in N₂ atmosphere (purity 99.99%) in a graphite furnace (HPW 150/200-2200-100-LA, FCT, Germany). Sintering temperature and time were varied between 1500°C and 1700°C, and between 2 h and 5 h, respectively. Heating and cooling rates were held constant at 10 K min⁻¹. Figure 1 shows an overview of the sample preparation process and the typical morphology of sintered samples.

### 2.2 Sample characterization

The shrinkage behavior of slip-cast materials was evaluated by dilatometry (Netzsch DIL 402 C), using a heating rate of 10 K min⁻¹ up to 1550°C in flowing N₂ atmosphere.

The density as well as apparent porosity of specimens was determined using the water immersion method, following EN 623-2. Mercury intrusion porosimetry was used to further evaluate the pore structure, including pore size distribution and pore opening diameter (Porotec Pascal 140/440; Hg contact angle: 140°, Hg surface tension: 0.48 N m⁻¹).

The microstructure and pore morphology were investigated by scanning electron microscopy (SEM; FEI Quanta 200). The relative phase content of starting powders and sintered samples was determined by x-ray diffraction analysis (XRD, X’Pert Pro, PANalytical with X’Celerator real-time multi strip detector; Cu Kα radiation, 2θ scanning range from 5° to 100°, 0.02° equivalent step size, 30 s equivalent counting time per step) in combination with Rietveld refinement (Highscore), using either powders (starting materials) or ground cross-sections (sintered samples).

The strength of materials was evaluated by a diametral compression test, using a C-ring setup for testing of tubular sections. Sections with a length of 5 mm were cut from tubular specimens using a diamond cut-off wheel. Subsequently, a narrow sector was cut in longitudinal direction, yielding test specimens with a C-shaped cross-section. The samples were tested in diametral compression using an electromechanical testing machine (Zwick 1474) at a cross-head speed of 0.5 mm min⁻¹. A minimum of 20 specimens were tested per batch, unless stated otherwise. The failure stress σ_c was calculated according to equations 1 and 2, involving the outer geometry of the specimen.

### Table 1

| Powder | d₅₀ (µm) | SSA (m² g⁻¹) | O content (wt%) | β-Si₃N₄ content (wt%) |
|--------|---------|--------------|----------------|-----------------------|
| E10    | 0.7     | 11.1         | 1.3            | 1.0                   |
| E03    | 1.1     | 3.1          | 0.7            | 0.3                   |
| XP06   | 1.2     | 6.2          | 0.6            | 11.1                  |

### Figure 1

(A) Processing scheme for slip casting of hollow-tube-shaped porous Si₃N₄ specimens; (B) Typical morphology and dimensions of sintered samples.
radius \( r_0 \), the wall thickness \( t \), the load at failure \( F \), the specimen length \( B \), the inner radius \( r_i \), and the mean radius \( r \), with \( r = (r_0 + r_i)/2 \):

\[
\sigma_c = \left[ \frac{(r_0 - 0.5 \cdot t) \cdot (r_0 - L)}{r_0 \cdot (r - L)} - 1 \right] \cdot \frac{F}{Bt} \tag{1}
\]

with

\[
L = \frac{t}{\ln(r_0/r_i)} \tag{2}
\]

The characteristic strength and Weibull modulus as well as the respective confidence intervals were determined using the maximum likelihood method, following EN 843-5.24

The gas permeability of samples was determined at room temperature using sintered tubular specimens, following a methodology reported previously.19,21 Filtered compressed air was used as fluid. The stationary permeating flow \( Q \) through the tube wall was determined at varying differential pressures \( \Delta p \) between feed and permeate, with \( \Delta p \) in the range between 0.2 and 3 bar. A minimum of three individual samples were tested per batch, with a typical number of five to eight sets of \( Q \) vs. \( \Delta p \) recorded per sample. Darcian \((k_1)\) and non-Darcian \((k_2)\) permeabilities were determined based on Forchheimer’s equation for compressible fluids (equation 3) by fitting a quadratic function to \( (p_i^2 - p_0^2)/(2\cdot p_0 \cdot l) \) versus \( Q/A \) using the least squares method.25

\[
\frac{p_i^2 - p_0^2}{2p_0 \cdot l} = \frac{\eta}{k_1} A + \frac{\rho}{k_2} \left( \frac{Q}{A} \right)^2 \tag{3}
\]

Here, \( p_i \) and \( p_0 \) are the absolute pressures at the feed and permeate side, respectively, \( l \) is the wall thickness, and \( A \) is the permeated area. An air viscosity of \( \eta = 1.84 \times 10^{-5} \) Pa s and an air density of \( \rho = 1.15 \) kg m\(^{-3} \) were assumed.

3 | RESULTS AND DISCUSSION

3.1 | Effect of sintering temperature

In a first step, the general shrinkage behavior of the Si\(_3\)N\(_4\)–Al\(_2\)O\(_3\)–Y\(_2\)O\(_3\) system was evaluated by dilatometry (Figure 2), using a starting powder consisting primarily of \( \alpha \)-Si\(_3\)N\(_4\) (E10). The onset of shrinkage at around 1390°C is in good accordance with data reported by Suttor and Fischman,17 who found densification of Si\(_3\)N\(_4\) in the presence of Al\(_2\)O\(_3\) and Y\(_2\)O\(_3\) as sintering aids to start at 1350°C, corresponding to the first evolution of a liquid phase. As mentioned previously, the presence of SiO\(_2\), introduced through oxygen impurities into the starting powder, has to be taken into account here: in case of the E10 powder used, an oxygen content of 1.3 wt% in the starting mixture (see Table 1) corresponds to an equivalent of 2.2 wt% of SiO\(_2\), this value approaching the content of admixed sintering aids. Consequently, the Al\(_2\)O\(_3\)–Y\(_2\)O\(_3\)–SiO\(_2\) phase system has to be considered, which exhibits a ternary eutectic at 1345°C according to the system’s phase diagram.17,26

To obtain a general overview of the effect of the sintering temperature in the interval between 1500°C and 1600°C on densification, mechanical properties, and permeability, a series of sintering experiments were conducted using the E10 starting powder. In this particular experiment, the sintering temperature interval was selected to result in total porosity values in the range from 30% to 40%, a porosity range expected to achieve a suitable combination of permeability and mechanical property characteristics, thus being typical for various support materials.

The resulting data are shown in Table 2. While total porosity is indirectly proportional to the temperature in this temperature range, the characteristic strength slightly increases, approaching a plateau value of around 150 MPa (Figure 3). As can be expected, gas permeability, particularly the Darcian contribution \((k_1)\), decreases with decreasing total porosity. The mean pore opening diameter determined by mercury intrusion porosimetry increases with rising sintering temperature, which can be traced to phenomena typically encountered during liquid phase sintering, foremost particle rearrangement.

In this particular series of experiments, the maximum temperature was limited to 1600°C. As sintering experiments carried out at higher temperatures showed further densification, the maximum sintering temperatures for subsequent investigations, involving, for example, the reduction in sintering aid content or the use of alternative starting powders, were conducted up to 1700°C.

3.2 | Effect of sintering aid content

As expected, the sintering aid content was found to significantly affect the densification behavior and, consequently, the microstructural and mechanical features. A systematic variation of
Al₂O₃ and Y₂O₃ contents between 0.2 wt% and 2.5 wt% carried out using the E10 powder variant of Si₃N₄ showed a straightforward relation between sintering aid content and densification, with final porosities ranging from 29% to 50% (Figure 4).

The development of the characteristic strength of specimens, determined by a strength screening with a reduced number of specimens of n_min = 7 (due to the fragile nature of specimens with low sintering aid contents), showed the expected indirect relationship between residual porosity and strength. As a consequence, sintering aid contents of 1 wt% and 2.5 wt% were selected for subsequent investigations, providing an adequate trade-off between porosity and strength.

### 3.3 | Effect of starting powder

While E03 and E10 starting powders primarily consist of α-Si₃N₄ (>99 wt%), the XP06 powder variant has an initial β-Si₃N₄ content of 12 wt%, according to XRD investigations. This significantly affects the conversion of α-Si₃N₄ to β-Si₃N₄ during sintering: after heat-treatment at 1600°C for 2 h (sintering aid content of 2.5 wt%), the β-fraction of total Si₃N₄ of E03, E10, and XP06 materials is 1.5 wt%, 27.9 wt%, and 98.6 wt%, respectively.

The three powders show significant differences in densification behavior, in pore structure evolution, and—consequently—in strength and permeability characteristics of the final materials (Figure 5). Full permeability results can be found in Table S1 in the Supplementary Information. In case of E03 and E10 powders, the difference in densification and resulting pore diameter can be related directly to the difference in starting particle size (see Table 1). In contrast, XP06, which nominally has an intermediate particle size (albeit appearing to exhibit a bimodal size distribution, see Figure S1 in the Supplementary Information), shows a significantly different behavior, resulting in both higher total porosity and larger median pore diameters. This can be traced to the aforementioned difference in initial composition, that is, a higher β-Si₃N₄ starting content, which affects the morphology of the resulting microstructure toward more anisotropic features (Figure 5), in contrast to equiaxed grains present in E03 and E10 materials. The change in morphology allows for a conservation of strength values even though total porosity is significantly increased in XP06 materials, whereas the permeability characteristics greatly benefit from increased porosity and pore diameter. This renders XP06 a highly interesting candidate material for further development.

### 3.4 | Iterative pore tailoring approach toward enhanced permeability characteristics

Based on the promising results of these systematic investigations illustrating the high suitability of XP06 powders toward...
**Figure 5** Effect of starting powder characteristics on (A) porosity and characteristic strength, and (B) median pore diameter and permeability, as well as (bottom) microstructural morphology of fracture surfaces (materials sintered for 2 h at 1600°C and 2.5 wt% sintering aid content).

**Table 3** Porosity, mean pore opening diameter, characteristic strength $\sigma_0$, Weibull modulus $m$, Darcian permeability $k_1$, and $\beta$-Si$_3$N$_4$-content as a function of sintering temperature, sintering time, and sintering aid content (XP06; ± values represent the standard deviation, bracket values represent the 95% confidence interval).

| Sample          | Porosity (%) | Mean pore diameter (µm) | $\sigma_0$ (MPa) | $m$   | $k_1$ (10$^{-15}$ m²) | $\beta$-Si$_3$N$_4$-content (wt%) |
|-----------------|--------------|-------------------------|-----------------|-------|-----------------------|----------------------------------|
| 1500°C, 2 h, 2.5%| 46.3 ± 0.2   | 0.23                    | 34.9 (30.4–40.0) | 3.9   | 1.73 ± 0.21           | 15                               |
| 1550°C, 2 h, 2.5%| 44.6 ± 0.3   | 0.25                    | 61.8 (50.8–74.9) | 2.6   | 1.97 ± 0.66           | 17                               |
| 1600°C, 2 h, 2.5%| 39.1 ± 0.5   | 0.44                    | 185.4 (144.4–236.9) | 2.0   | 1.76 ± 0.09           | 99                               |
| 1600°C, 5 h, 2.5%| 32.3 ± 0.6   | 0.49                    | 188.0 (166.9–211.4) | 4.5   | 1.63 ± 0.07           | 92                               |
| 1600°C, 5 h, 1.0%| 44.5 ± 0.4   | 0.53                    | 147.9 (130.8–166.9) | 4.1   | 3.13 ± 0.27           | 92                               |
| 1700°C, 5 h, 1.0%| 41.1 ± 0.2   | 0.74                    | 163.1 (153.1–173.5) | 8.0   | 4.71 ± 0.65           | 92                               |

**Figure 6** Fracture surfaces of Si$_3$N$_4$ specimens obtained from XP06 powder after sintering at (A) 1500°C, (B) 1550°C, and (C) 1600°C (sintering time 2 h and sintering aid content 2.5 wt%).
combining suitable mechanical strength with excellent permeability values, the combined effect of a variety of parameter variations was investigated for this starting material. The overall results are presented in Table 3.

In the first iteration, the effect of the sintering temperature on the resulting material characteristics of XP06 powder was evaluated, using parameter variants shown to be suitable for E10 powders (as described in previous sections), including a sintering aid content of 2.5 wt% and a sintering time of 2 h.

For this particular powder variant, and in contrast to previous experiments with E10 powder, sintering temperatures below 1600°C resulted in inadequate densification, yielding high total porosities and, consequently, decreased mechanical properties. Sintering at 1600°C, in contrast, was found to result in significantly increased characteristic strength values of 185 MPa, in spite of samples retaining a rather high total porosity of 39%. Furthermore, the mean pore diameter of up to 0.5 µm was found to be significantly larger than in case of E10 powders, which in combination with increased total porosity resulted in significantly improved gas permeability characteristics (approaching a $k_1$ value of $1.8 \cdot 10^{-15}$ m²). Corresponding to a five-fold increase when compared to the E10 variant. The remarkable change in material behavior upon raising the sintering temperature from 1550°C to 1600°C could be correlated with changes in the crystalline phase composition, showing an increase in the relative $\beta$-Si$_3$N$_4$ phase content from 17% to nearly 99%, thus directly affecting the microstructure of the material (Figure 6).

In order to promote further enhancement of the permeability, the next iteration step included an increase in sintering time from 2 h to 5 h, with the aim to further modifying pore openings toward improved gas flow. For the starting composition with a sintering aid content of 2.5 wt%, this resulted in a significant decrease in total porosity to 32%, thus effectively counteracting these efforts. By decreasing the sintering aid content to 1 wt%, however, it was possible to reach a total porosity above 44% and, in combination with a slight increase in mean pore opening diameter, a doubling of permeability. While the characteristic strength was expected to slightly decrease in this case, the extent of structural weakening was surprisingly low.

Nonetheless, in order to further counteract this decrease in mechanical strength, an increase in sintering temperature to 1700°C was evaluated in the final iteration. By choosing this combination of starting composition and sintering parameters, the mean pore opening diameter was increased to 0.8 µm, while retaining a characteristic strength of 163 MPa, a value more than ten times higher than for specimens obtained from E10 powder with comparable mechanical properties. The evolution of microstructural features upon the applied modifications of sintering parameters is shown in Figure 7.

Figure 8 highlights the primary outcome of our iterative process development approach toward enhanced gas permeability characteristics for Si$_3$N$_4$ materials. By careful consideration and identification of critical process parameters such as starting powder composition and morphology, sintering temperature, sintering time, and sintering aid content, well-tailored microstructures were designed providing a sixfold increase in gas permeability while at the same time largely retaining total porosity, and even increasing characteristic strength.

In terms of permeability characteristics, a significant effect of the pore structure on the respective contributions of viscous and inertial resistance on the pressure drop was found, which can be derived from $k_1$ and $k_2$ via the dimensionless Forchheimer number $F_0$. While the pressure drop at higher flow velocities was dominated by inertial resistance in samples with spherical grains and more finely featured pores (e.g., sample E10-1500°C-2h-2.5% in Figure 8), the gas flow characteristics in materials with microstructures exhibiting larger, elongated grains (e.g., sample XP06-1700°C-5h-1% in Figure 8) were largely determined by viscous resistance. A more detailed evaluation of the relative contributions of viscous and inertial resistance for selected samples can be found in the Supplementary Information (Table S2).

Based on findings from previous investigations, for example, by Topates et al., it can be assumed that even higher permeabilities may be achieved when using coarser starting powders, a variation not being the focus of this present work. However, a corresponding comparison with strength data...
reported in the literature for partially sintered Si₃N₄ materials (as reported, e.g., by Kalemtas et al.¹²) is generally difficult due to significant methodological differences in testing setups (i.e., flexural vs. diametral compression testing). In this case, the respective mechanical stress scenarios to be expected during the prospective operation have to be considered.

4 | CONCLUSIONS

The results of this study demonstrate the effect of material- and process-specific parameters for systematically tailoring the macropore structure of partially sintered Si₃N₄ structures toward facilitating excellent gas flow while, at the same time, preserving mechanical characteristics required for prospective application as porous supports.

By selecting a Si₃N₄ powder variant with an increased β-Si₃N₄ starting content, the α → β conversion taking place during thermal treatment can be promoted significantly, resulting in an elongated grain morphology shown to be highly beneficial in terms of flow characteristics and mechanical properties. In a more straightforward manner, the resulting microstructure can be tailored through careful and balanced control of conventional sintering parameters such as temperature and time, as well as by the amount of additives facilitating liquid-phase sintering. Both an increase in sintering temperature and sintering time leads to pore coarsening, thus positively affecting transverse flow. In order to counteract the
increased tendency toward densification under these conditions, a reduction in the relative content of sintering additives can be used to preserve total porosity values, thus leading to a combination of large pore diameters, high porosity, and suitable mechanical strength, rendering these materials ideal candidates for typical application scenarios in the fields of filtration, catalysis, or membrane-based separation.

ACKNOWLEDGMENTS
This work was supported by the Austrian Science Fund (FWF): P29058. J. Rauchenecker and J. Eßmeister are gratefully acknowledged for their support in XRD investigations.

ORCID
Thomas Konegger © https://orcid.org/0000-0002-0454-5062

REFERENCES
1. Ohji T, Fukushima M. Macro-porous ceramics: processing and properties. Int Mater Rev. 2012;57(2):115–31.
2. Scheffler M, Colombo P. Cellular Ceramics. Weinheim: Wiley-VCH Verlag; 2005.
3. Klemm H. Silicon nitride for high-temperature applications. J Am Ceram Soc. 2010;93(6):1501–22.
4. Chen F, Shen Q, Yan F, Zhang L. Pressureless sintering of α-Si3N4 porous ceramics using a H3PO4 pore-forming agent. J Am Ceram Soc. 2007;90(8):2379–83.
5. Konegger T, Patidar R, Bordia RK. A novel processing approach for free-standing porous non-oxide ceramic supports from polycarbosilane and polysilazane precursors. J Eur Ceram Soc. 2015;35(9):2679–83.
6. Chen D, Zhang B, Zhuang H, Li W. Combustion synthesis of network silicon nitride porous ceramics. Ceram Int. 2003;29(4):363–4.
7. Fukasawa T, Deng Z-Y, Ando M, Ohji T, Kanzaki S. Synthesis of porous silicon nitride with unidirectionally aligned channels using freeze-drying process. J Am Ceram Soc. 2002;85(9):2151–5.
8. Xia Y, Zeng Y-P, Jiang D. Microstructure and mechanical properties of porous Si3N4 ceramics prepared by freeze-casting. Mater Des. 2012;33:98–103.
9. Li X, Yao D, Zuo K, Xia Y, Yin J, Liang H, et al. Fabrication, microstructural characterization and gas permeability behavior of porous silicon nitride ceramics with controllable pore structures. J Eur Ceram Soc. 2019;39(9):2855–61.
10. Yue J, Dong B, Wang H. Porous Si3N4 fabricated by phase separation method using benzoic acid as pore-forming agent. J Am Ceram Soc. 2011;94(7):1989–91.
11. Yu J, Yang J, Li H, Huang Y. Pore structure control of Si3N4 ceramics based on particle-stabilized foams. J Porous Mater. 2012;19(5):883–8.
12. Kalemtas A, Topates G, Özcoban H, Mandal H, Kara F, Janssen R. Mechanical characterization of highly porous β-Si3N4 ceramics fabricated via partial sintering & starch addition. J Eur Ceram Soc. 2013;33(9):1507–15.
13. Mori H, Mase S, Yoshimura N, Hotta T, Ayama K, Tsubaki JL. Fabrication of supported Si3N4 membranes using the pyrolysis of liquid polysilazane precursor. J Membr Sci. 1998;147(1):23–33.
14. Salmang H, Scholze H. Keramik. Berlin, Heidelberg: Springer-Verlag; 2007.
15. Almeida JC, Fonseca AT, Correia RN, Baptista JL. Pressureless sintering of silicon nitride with additives of the Y2O3-Al2O3-SiO2 system. Mater Sci Eng A. 1989;109:395–400.
16. Yang J-F, Ohji T, Niihara K. Influence of yttria-alumina content on sintering behavior and microstructure of silicon nitride ceramics. J Am Ceram Soc. 2000;83(8):2094–6.
17. Sutter D, Fischman GS. Densification and sintering kinetics in sintered silicon nitride. J Am Ceram Soc. 1992;75(5):1063–7.
18. Topates G, Mammitzsch L, Petasch U, Adler J, Kara F, Mandal H. Microstructure–permeability relation of porous β-Si3N4 ceramics. J Eur Ceram Soc. 2013;33(9):1545–51.
19. Konegger T, Prochaska T, Obmann R. Tubular ceramic structures from polymer precursors with controlled porosity, strength, and permeability characteristics. J Ceram Soc Jpn. 2016;124(10):1030–4.
20. Li K. Ceramic Membranes for Separation and Reaction. Chichester: Wiley; 2007.
21. Brouczek D, Konegger T. Open-porous silicon nitride-based ceramics in tubular geometry obtained by slip-casting and gelcasting. Adv Eng Mater. 2017;19:1700434.
22. European Standard EN 623. Advanced technical ceramics; Monolithic ceramics – general and textural properties; Part 2: Determination of density and porosity: EN 623-2; 1993.
23. Munz D, Fett T. Ceramics: Mechanical Properties, Failure Behaviour, Materials Selection. Berlin: Springer-Verlag; 1999.
24. European Standard EN 843. Advanced technical ceramics; Mechanical properties of monolithic ceramics at room temperature – Part 5: Statistical Analysis: EN 843-5; 2006.
25. Innocentini M, Sepulveda P, Ortega F. Permeability. In Scheffler M, Colombo P (editors). Cellular Ceramics. Weinheim: Wiley-VCH; 2005:313-41.
26. Levin EM, Robbins CR, McMurdie HF. Phase Diagrams for Ceramists, 1969 Supplement. Columbus: The American Ceramic Society; 1969.

SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section.

How to cite this article: Konegger T, Prochaska T, Brouczek D. Porosity control in silicon nitride-based support materials toward enhanced gas permeability. Int J Appl Ceram Technol. 2021;00:1–9. https://doi.org/10.1111/ijac.13803