Preparation of hollow fiber membranes from mullite particles with aid of sintering additives

Hua LIU^a, Jinyun LIU^a, Zhou HONG^b, Shengxian WANG^a,
Xuechao GAO^{a,*}, Xuehong GU^{a,*}

^aState Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, No. 30 Puzhu Road (S), Nanjing 211816, China

^bNanjing Membrane Materials Industrial Technology Research Institute Co., Ltd.,
No. 1 Yuansi Road, Pukou Economic Development Zone, Nanjing 211808, China

Received: May 16, 2020; Revised: August 25, 2020; Accepted: September 4, 2020

© The Author(s) 2020.

Abstract: Porous mullite hollow fiber membranes were prepared with a combined phase-inversion and sintering method, using three sintering additives including yttrium stabilized zirconia (YSZ), small mullite particles (SMP), and titanium oxide (TiO₂) to promote the particle sintering. The results indicated that all the three additives could improve the sintering performance of mullite hollow fiber membranes due to the decrease in activation energy of mullite grains. Both YSZ and TiO₂ could react with mullite grains to generate composite oxides (e.g., ZrSiO₄ and Al₂TiO₅) during sintering, following a reaction-sintering mechanism. Interestingly, the newly generated ZrSiO₄ was instable and further decomposed into monoclinic ZrO₂ and SiO₂ in the sintering process. The decomposition could avoid excessive embedment of composite oxides among mullite grains which have negative impact on mechanical strength of mullite hollow fibers. Overall, the doping of YSZ provided a better promotion effect on the sintering of mullite hollow fiber membranes, where the microstructural and mechanical properties are insensitive to the doping content and sintering temperatures, so it could be used as the candidate for the large-scale preparation of mullite hollow fibers.

Keywords: mullite; sintering additives; hollow fiber; membranes; sintering behavior

1 Introduction

Ceramic membranes behave high thermo-chemical resistance and were suitable for the separation in harsh environments, such as high temperature and strong solvents. Ceramic membranes are mainly made from the inorganic materials such as alumina [1], zirconia

[2], and titania [3], and the commercial products are fabricated as flat sheet and tube. Compared with the large tube used in the membrane fabrication, hollow fiber structured ceramic membranes have attracted great attentions due to their ultra-high area/volume ratios and low transfer resistance, where the membrane system could be significantly reduced for the practical application of separation processes [4,5]. Phase-inversion method is often used to prepare the ceramic hollow fiber membranes [1,6,7], and a higher permeability could be derived due to its asymmetric structure [1].

* Corresponding authors.

E-mail: X. Gao, xuechao.gao@njtech.edu.cn;

X. Gu, xhgu@njtech.edu.cn

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is one of the aluminosilicate ceramic materials, which has the advantages of low thermal expansion coefficient, high mechanical strength, good chemical stability, excellent thermal shock resistance and creep resistance [8–11]. Industrially, mullite ceramic is produced mainly from various raw mineral materials, such as kaolin [12–15], bauxite [11,12,16,17], coal gangue [11,18], clay [13,19], and topaz sand [20]. Due to the high abundance of the raw mineral materials, mullite could be regarded as an excellent candidate for the fabrication of porous hollow fiber ceramic membranes.

Up to date, the report on the preparation of mullite hollow fiber membranes was very limited. Dong and his coworkers prepared mullite hollow fiber membranes from mineral materials such as bauxite powder and ball clay by reaction sintering technique [17,21]. It was observed that the mullite volume tended to increase largely as the sintering temperature increased from 1250 to 1450 °C [22], which could generate large voids in the bulk mullite. The mullite membranes fabricated from coal gangue and bauxite can undergo an abnormal volume expansion, primarily due to occurrence of secondary mullitization followed by the rapid anisotropic growth of mullite crystals [11,12]. The second stage of mullitization would cause large voids and tube deformation during the sintering process. To address the issue, it is encouraged to prepare mullite membranes directly from mullite powder. However, mullite powder is difficult to be sintered together, due to the low diffusion rates of the aluminum and silicon species [12,23]. Therefore, high sintering temperatures (> 1600 °C) are often required to obtain sufficient mechanical strength for the product of mullite ceramics [24].

Doping small-particle metal oxide additives in membranes has been found to be effective for promoting the $\alpha\text{-Al}_2\text{O}_3$ membranes sintering by the bridging of medium fine between coarse grains [25,26]. Thus, it is possible to reduce the sintering temperature of mullite membranes by adding suitable sintering additives in the membranes. In this work, we attempted to prepare mullite hollow fiber membranes directly from green mullite powder by phase-inversion and sintering method. Three additives including yttrium stabilized zirconia (YSZ), small mullite particles (SMP), and titanium oxide were compared in order to improve the sintering performance of mullite hollow fiber membranes. Extensive characterizations were performed to understand the sintering behavior of mullite hollow fiber membranes

doped with the additives. It was shown that high mechanical strength of mullite hollow fibers could be prepared at a reduced sintering temperature.

2 Material and methods

2.1 Materials

Commercially available mullite powder was used as the membrane material, which has a mean particle size (d_{50}) of ~ 4.4 μm . 8 mol% YSZ, SMP, and titanium oxide (TiO_2 , rutile) with the similar particle size (~ 1 μm) were used as the sintering additives. Polyethersulfone (PESf), N-methyl-2-pyrrolidone (NMP), and polyvinylpyrrolidone (PVP, K30) were used as the binder, solvent, and dispersant, respectively. Deionized water and tap water were used as internal and external coagulants, respectively. All the chemicals are industrial grade, which were obtained from commercial companies in China.

2.2 Preparation of mullite hollow fiber membranes

Mullite hollow fiber membranes were prepared via the dry-wet spinning method followed by a high temperature sintering. PESf, PVP, and NMP were mixed at required quantities to form a polymer solution, and then a certain amount of sintering additive (YSZ, SMP, or TiO_2) was added into the polymer solution under constant stirring (~ 300 rpm) for 1 h to yield a homogeneous solution. Subsequently, a certain amount of mullite powder was added into the solution with vigorous stirring for 24 h, to obtain a homogeneous spinning solution. The suspension has a mass ratio of ceramic materials:PESf:NMP:PVP=0.530:0.106:0.347:0.017. The mass fractions of sintering additives/(mullite + sintering additives) were 0.05, 0.10, 0.15, and 0.20, respectively. The prepared suspension was degassed using a vacuum pump to remove air bubbles. Then, the suspension was immediately transferred into a 200 mL stainless-steel syringe. The ceramic suspension was extruded through the spinneret by syringe pumps at a constant flow rate of 50 mL/min at room temperature. The structural design of the four-channel spinneret has been described in our previous work [27]. The air-gap was kept at 10 cm, and the flow rate of de-ionized water (internal coagulant) was controlled at 40 mL/min for all spinning processes. The precursors were immersed in the external coagulant for 24 h to ensure the com-

pletion of phase inversion process. After being dried at room temperature, the hollow fiber precursors were sintered in air using a high-temperature furnace for 5 h, where the setting temperature was varied between 1520 and 1630 °C.

2.3 Characterizations

The morphologies of mullite hollow fiber membranes were observed by the scanning electron microscopy (SEM, S4800, Hitachi). The phase composition of the sintered fibers was determined by X-ray diffraction (XRD, MiniFlex 600, Rigaku) with a Cu K α radiation source in the 2 θ range of 5°–80°. All the fracture load tests of the mullite hollow fiber membranes were performed by an electronic universal testing machine (UTM6103, Shenzhen Suns Technology Stock Co., Ltd.) with a span of 40 mm, where the cross-head speed in the monotonic test was 0.5 mm/min. The mean pore size of the fibers was measured by micro-filtration membrane pore-size analyzer (PSDA-20, GaoQ Functional Materials Co., Ltd.) based on the gas–liquid replacement mechanism [16]. Pure water flux was examined under a trans-membrane pressure of 0.1 MPa in which one end of the hollow fiber membrane was blocked with epoxy resin. The pure water flux was calculated according to the following equation:

$$Q = \frac{V}{A \cdot t} \quad (1)$$

where Q , V , A , and t are the pure water flux ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$), the total pure water permeation volume (m^3), the effective membrane area of the hollow fiber (m^2), and the measurement duration (h), respectively. The porosities of the fibers were determined with Archimedes method.

3 Results and discussion

3.1 Pure mullite hollow fiber membranes

Table 1 shows the performance of pure mullite hollow fiber membranes sintered at different temperatures for 5 h. As suggested, the fracture load of the sintered fibers increased with the increase in sintering temperatures. However, all the fibers exhibited relatively low fracture loads (< 7 N), as compared with four-channel Al_2O_3 hollow fiber membranes reported in our previous work, where a high value of more than 18 N could be derived [27,28]. This is mainly due to the

inherent property of mullite powder which behave low diffusion rates of the aluminum and silicon species in sintering processes [12,23]. Besides, the large particle size of mullite grains (4.4 μm) also required a higher sintering temperature than $\alpha\text{-Al}_2\text{O}_3$ samples with a particle size of 0.8 μm as used in our previous work [27,28]. As a result, the pore size of the membranes was quite large, which even exceeded the measure limit of the pore-size analyzer for the membranes sintered at 1520 and 1570 °C. Besides, the pure water flux of mullite hollow fiber membranes increased with sintering temperatures, under the conditions of a slightly reduced porosity and mean pore size at high temperatures. This was largely due to the consumption of SiO_2 and Al_2O_3 residuals by the reforming reaction at high temperature, where more narrow spaces were generated between the structural particles [4] and thus improved the continuity or connectivity of the interstitial pores in the membranes. The increase in pore connectivity leads to the enhancement of permeation flux of water due to the decrease in the apparent tortuosity of the porous media, according to the specific explanation in the literatures [29–31].

Figure 1 shows the SEM images of mullite hollow fiber membranes before and after sintering at 1520–1630 °C. As given in Fig. 1(a), the green hollow fiber before sintering had dense and smooth surfaces with mullite particles embedded in the polymeric phase. After sintering at 1520, 1570, and 1630 °C, the membranes contained porous structure, as shown in Figs. 1(b), 1(c), and 1(d), respectively. It was observed that the mullite grains fused with each other and plenty of neck connects were found. The increase in temperature is beneficial to the grain binding. However, the fusion of structural grains was still insufficient even for the highest sintering temperature of 1630 °C, as some isolated grains were still detected in the bulk. This explained why the hollow fiber membranes had low fracture load at a sintering temperature of 1630 °C. The sintering time was further extended for 8 h at 1630 °C, but the mechanical strength of hollow fiber membranes

Table 1 Measured properties of pure mullite hollow fiber membranes sintered at different temperatures for 5 h

Sintering temperature (°C)	Porosity (%)	Pure water flux ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	Mean pore size (μm)	Fracture load (N)
1520	58.63	40.98	—	2.91
1570	57.07	41.77	—	3.25
1630	55.88	53.59	0.956	6.81

Fig. 1 SEM images of (a) green mullite hollow fiber membrane, and its sintered products obtained under different temperature: (b) 1520 °C, (c) 1570 °C, and (d) 1630 °C.

was still very weak (below 10 N). To improve the mechanical strength of mullite hollow fiber membranes, sintering additives (YSZ, SMP, and TiO_2) were doped into the suspension.

3.2 Effects of different sintering additives

3.2.1 Membrane morphologies

Based on a sintering temperature of 1570 °C, the sintering additives of YSZ, SMP, and TiO_2 were adopted to explore the sintering enhancement effect of

mullite hollow fiber membranes, where the percentage of the sintering additive was adjusted as 5.0, 10.0, and 15.0 wt%, respectively. As suggested, compared with the pure mullite hollow fiber membrane in Fig. 1(c), the neck-connected areas of all the doped samples were enhanced according to the SEM images in Fig. 2. It is noticed that the sintered surface morphologies of the membranes varied with additive types. For instance, for a 5.0 wt% dosage of YSZ, SMP, and TiO_2 additives (represented by Figs. 2(a1), 2(b1), and 2(c1), respectively), the surface of the SMP-derived membrane was significantly denser than the result by YSZ or TiO_2 doping, for the voids between large mullite grains were filled by SMP additives. The additive content is also an important factor to account for the enhancement effect. For YSZ additives with different percentages in Figs. 2(a1)–2(a3), the fusion performance of mullite grains was improved with contents, i.e., the necks became more and more closely connected. For the SMP additive in Figs. 2(b1)–2(b3), the membrane surface also became more compactly at higher contents due to a better arrangement of mullite grains, but only a limited number of neck-connected areas were found. For TiO_2 doping in Figs. 2(c1)–2(c3), although no significant changes occurred to the three contents, the large voids embedded in the bulk of the membrane

Fig. 2 SEM images of mullite hollow fiber membranes doped with different additives and contents sintered at 1570 °C: (a) YSZ, (b) SMP, (c) TiO_2 , (1) 5.0 wt%, (2) 10.0 wt%, (3) 15.0 wt%.

were minimized and the neck connecting effect were found in all content levels. The above observations suggested that the promotion mechanism varied with sintering additives. Compared with SMP, YSZ, and TiO_2 had a better promotion on the sintering promotion of mullite hollow fiber membranes due to the solid-state reaction between the additives and mullite particles, in a different reaction mechanism for each type.

3.2.2 Mechanical strength

Since the sintering mechanism varies with additive types, it is necessary to systematically examine the commonly-used microstructure and mechanical properties of the membrane to provide guidance for the optimization of the membrane qualities. Figure 3 shows the effect of additive contents on the fracture load of the mullite hollow fiber membranes, after sintering at 1570 °C for 5 h. Compared with the pure hollow fiber membrane, all the doped samples exhibited enhanced fracture loads. For instance, at a 5 wt% additive content, the fracture load of the YSZ and TiO_2 doped samples increased by more than 6 times, being above 19 N, which was supplemented by a much smaller increase for the SMP-derived sample, being around 5 N. In addition, the YSZ content had a slight effect on the fracture load of the fibers, where the fracture load fluctuated between 21 and 22.8 N at different YSZ contents. Although both YSZ and TiO_2 involve a solid-state reaction mechanism, as shown in Fig. 2, a different variation of doping contents occurred to the TiO_2 additive, i.e., the fracture load decreased with the increase in TiO_2 content. For the fibers doped with SMP, higher content could enhance the fracture load of the fibers, where the highest was even reached up to

Fig. 3 Effects of the additive contents on the fracture load of the mullite hollow fiber membranes sintered at 1570 °C.

12.6 N, for a SMP content of 20 wt%. Since SMP is the mullite material with smaller particle size, the enhanced mechanical strength was mainly attributed to the increases in contact area between mullite particles, which increased with doping percentage. The difference in enhancement of fracture loads suggested that the solid-state reaction provided stronger binding forces than the increase in contacting areas between mullite particles.

3.2.3 Microstructural properties

Figure 4 depicts the effect of additive content on the porosity of the mullite hollow fiber membranes doped with the three additives, after sintering at 1570 °C for 5 h. As suggested, the porosity of fibers decreased with the increase in the content of YSZ and SMP additives, where a significant drop from 44.2% to 31.8% occurred for the YSZ content from 5.0 wt% to 20 wt%, which was supplemented by a much milder decrease from 53.9% to 49.3% at the same variation for SMP additive. On the contrary, the porosity of TiO_2 -doped samples demonstrated a different behavior, which started as an initial increase before stabilizing at around 45%, being exceeded the value derived by YSZ doping. The different response of the porosity to TiO_2 doping content has caused the decrease in mechanical strength as shown in Fig. 3.

Figure 5 shows the effect of additive content on the mean pore size and pure water flux of the mullite hollow fiber membranes. With the increase in SMP content, both the mean pore size and pure water flux decreased as the membrane surface became more compactly due to the improved arrangement of the mullite grains. On the contrary, the enrichment of TiO_2 content yielded a slightly increase in the mean pore size and pure water flux due to the reaction between

Fig. 4 Effects of the additive contents on the porosity of the mullite hollow fiber membranes sintered at 1570 °C.

Fig. 5 Effects of additive contents on (a) mean pore size, and (b) pure water flux of mullite hollow fiber membranes sintered at 1570 °C.

TiO₂ and mullite, which generated more vacancies between the structural particles [4]. For the YSZ-doped fibers, the mean pore size of mullite hollow fiber membranes was enlarged by the increase in YSZ content from 5.0 wt% to 15 wt%, before turning into a decrease when the YSZ content increased to 20 wt%. Meantime, the pure water flux decreased with YSZ content from 5.0 wt% to 20 wt% due to the competitive interplay between the pore connectivity/tortuosity and the pore size.

3.3 Mechanism explanation

The differences in tendencies of the mechanical and microstructural properties (fracture load, porosity, pore size, and water flux) versus the doping content confirmed the previous assumption based on SEM images that the mechanism to promote the sintering of mullite hollow fiber membranes varies with additive types. To further explore the sintering mechanism among the three sintering additives, XRD characterizations were used to examine the crystal structure of sintered membranes doped with 20 wt% additives, which could yield the strongest signal for any structural alteration in the crystal lattice. As mentioned above, the diffusion rate of the aluminum and silicon species is very low, so a high activation energy (~700 kJ/mol) is expected for the bridging of mullite grains. Thus, to promote the sintering of mullite hollow fiber membranes, the activation energy of mullite grain must be reduced or overcome by the presence of additives acting in different manners.

When using SMP as an additive, only mullite phase was found in the sintered hollow fibers. Compared with mullite powder (~4.4 μm), the surface free energy of the SMP additive (~1.0 μm) is sufficiently large, so the activation energy of sintering was reduced, and the promotion of mullite hollow fiber membranes

increased with the addition of SMP. The small particles were more easily fitted in the space confined by large mullite particles, so the porosity and mean pore size of the fibers slightly decreased with SMP contents. Since no solid-reaction between mullite particles involved in the sintering process, the inter-connect/penetration between particles was very limited, so the fracture load of the SMP-derived sample was still weak for the low doping content, in spite of a much denser surface of the membrane, as suggested by the SEM images in Fig. 2.

For TiO₂ doping, Al₂TiO₅ phase could be generated in the sintering process, indicating the occurrence of solid-state reaction/connecting between TiO₂ and mullite (Fig. 6). In this process, Ti⁴⁺ substituted of Al³⁺ in the mullite lattice to enhance the diffusivity rate of atoms in the crystal lattice [28], thereby improving the inter-penetration between mullite grains. Since the TiO₂ phase was hardly detected in the sintered hollow fiber doped with 20 wt% TiO₂ and sintered at 1520 °C, a complete transformation of TiO₂ to Al₂TiO₅ was expected in the sintering process. As the total volume

Fig. 6 XRD patterns of (a) 20 wt% TiO₂ doped mullite hollow fiber membranes at 1520 °C, and its related standards: (b) rutile TiO₂ standard, (c) Al₂TiO₅ standard, (d) mullite standard.

of ceramic powder remained almost unchanged, the consumption of TiO_2 generated vacancies among the structural particles, thereby leading to an increase of porosity, mean pore size, and pure water flux. Figure 7 displays the relative intensity of Al_2TiO_5 obtained from XRD patterns as a function of TiO_2 content for the fibers sintered at 1630°C . To track the content of Al_2TiO_5 , the relative intensity is defined as the height ratio of the strongest peak of Al_2TiO_5 at 18.80° over that of mullite at 25.97° in the XRD pattern. It is suggested that the relative intensity of peak ratio demonstrated a strong dependence on the TiO_2 content, which could be correlated to estimate the relative content of the Al_2TiO_5 when only mullite and Al_2TiO_5 are present in the fibers. An increased percentage of Al_2TiO_5 was confirmed for our samples, which explained the reduced mechanical strength at a higher content of TiO_2 additive in Fig. 3. At high temperatures, the Al_2TiO_5 with weak mechanical properties [32,33], was liquidized to promote inter-penetration between mullite particles. However, its excessive presence impedes travel between neighboring mullite grains, as a longer path involves. Therefore, the sintering additive of TiO_2 should be explored at a low content to promote the sintering of mullite hollow fibers. In view of the difficulty to uniformly disperse low quantity of solids in the spinning solution, this additive is inconvenient for the large-scale production of mullite hollow fibers.

Figure 8 depicts the phase analysis of XRD patterns for the pure mullite powder, YSZ-doped mullite hollow fiber membrane, and pure YSZ powder sintered at 1630°C . As suggested, when YSZ was doped into the mullite powder, the peaks of monoclinic ZrO_2 (m- ZrO_2) was found in the fiber, but, by contrast, no m- ZrO_2 phase

Fig. 7 Effects of TiO_2 content on the relative intensity of Al_2TiO_5 for the fibers sintered at 1630°C .

Fig. 8 XRD patterns of (a) mullite powder, (b) YSZ powder, (c) 20 wt% YSZ/mullite hollow fiber membranes sintered at 1630°C , respectively, (d) tetragonal ZrO_2 standard and (e) mullite standard ($\blacktriangle$: monoclinic ZrO_2 , $\bullet$: α - Al_2O_3).

was detected for the pure YSZ powder sintered at the same temperature, so the transformation of m- ZrO_2 was confirmed due to the solid-reaction between the YSZ additive and mullite grains. Interestingly, no product could be defined to confirm the solid-reaction between the YSZ additive and mullite grains. The XRD characterization proved that YSZ-doped membranes have a different sintering manner from the fibers doped with the others, and the schematic mechanism was depicted in Fig. 9. As shown, the t- ZrO_2 in YSZ particles could react with SiO_2 in mullite grains to generate the intermediate product of zircon; followed by a decomposing reaction, the particles of m- ZrO_2 , SiO_2 , and Al_2O_3 were derived [34,35]. The obtained SiO_2 and Al_2O_3 have smaller sizes and could be reassembled to inter-connect with the dispersed mullite grains in a similar manner to the SMP additive, so the corresponding porosity exhibited a similar trend versus the content to that doped with SMP. This explanation was further supported by the work of Mahnicka-Goremikina *et al.* [36], where the particle size of mullite grains in the ZrO_2 -doped samples became smaller than that in the pure sample. Due to the occurrence of stronger solid-state reaction/inter-penetration between mullite grains and YSZ particles, the high mechanical strength of the doped membrane could be maintained under different contents, suggesting a wider tolerance for the large-scale production of mullite hollow fibers.

3.4 Effects of sintering temperature on YSZ-doped fibers

As discussed above, YSZ grains exhibited an advantage of content insensitivity in assisting the sintering of

Fig. 9 Schematic diagram of sintering process for mullite particles doped with YSZ.

mullite hollow fiber membranes over the SMP and TiO_2 additives for the large-scale production, so it is meaningful to systematically investigate the effect of sintering temperature on the membrane properties in order to optimize its doping conditions. As low contents could provide sufficient strength for the YSZ-doped hollow fibers, YSZ-doped fibers at 5 wt% were sintered using the temperatures of 1520, 1570, and 1630 °C to collect the variation of mechanical and microstructural properties. The results and its comparison with the values in the literature are summarized in Table 2. As expected, the prepared fibers in current work exhibited small variations of microstructural and mechanical properties in a wide range of sintering temperature, and the comprehensive performance of the doped membrane was consistently higher than the results reported in the literatures. For instance, in terms of the permeation flux of water, a slight increase occurred with the temperature increasing, and the highest value was about $60.77 \text{ m}^3/(\text{m}^2 \cdot \text{h})$, being much higher than the competitor with a value of $1.29 \text{ m}^3/(\text{m}^2 \cdot \text{h})$ at a sintering temperature of 1250 °C [37]. Mechanical strength is another important parameter to ceramic hollow fibers. It is seen that the fracture load of the prepared fibers exhibited a high fracture load of 23.21 N. This value is lightly lower than the competitor with a value 28.34 N reported by Li *et al.* [17], which is

possibly due to a longer span (40 mm) used in this work compared with the competitor (8 mm). The above results indicated that YSZ additive also had a wide operating zone for the sintering temperature (1520–1630 °C), which constituted another advantage for the large-scale preparation of mullite hollow fiber, where the effect of the temperature profile in the furnace chamber on the membrane qualities could be minimized.

4 Conclusions

Analysis of mullite hollow fiber membranes prepared under the assistance of YSZ, TiO_2 , and SMP additives indicated that all the three additives could enhance the mechanical strength of mullite hollow fiber membranes by improving the inter-connects of the mullite grains in different manners. The promotion mechanism for the SMP additive is largely dominated by high surface free energies and contacting areas of small particles, so the enhancement of the mechanical strength for the doped membrane is limited, in spite of a denser membrane surface. Solid-state reaction is confirmed in both YSZ and TiO_2 doping, so the enhancement is much more significant, where the intermediate products of zircon and Al_2TiO_5 were yielded for each additive, respectively. Compared with the stable state of Al_2TiO_5 in TiO_2 doping, zircon in YSZ doping could be easily decomposed into m- ZrO_2 and SiO_2 at high temperature, which could be reassembled to inter-connect mullite grains after reacting with Al_2O_3 residuals. Since the inhibition effect of sintering due to the excessive embedment of intermediate composite was avoided for YSZ doping, the high mechanical and microstructural properties of the doped membrane were adequately maintained in the wide content of additive, which facilitates the large-scale preparation of the hollow fibers. To further optimize the temperature effect on the membrane performance for the YSZ additive, a low

Table 2 Performances of mullite hollow fiber membranes

Sintering temp (°C)	Porosity (%)	Pure water flux ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	Mean pore size (μm)	Span (mm)	Fracture load (N)	Ref.
1520	51.86	47.7	1.16	40	21.7	This work
1570	46.11	50.06	1.53	40	21.5	This work
1630	46.23	60.77	1.47	40	23.21	This work
1250	50.50	1.29	0.61	43	2.74*	[37]
1350	—	—	0.90	8	28.34*	[17]

*The fracture load in the reference was estimated based on the flexural strength supplied in literature.

content of 5 wt% YSZ was systematically explored by varying the sintering temperature from 1520 to 1630 °C. The results demonstrated YSZ-derived hollow fiber membranes had another significant advantage of temperature insensitivity in terms of the mechanical and microstructural properties, as the effect of temperature profile in the sintering furnace on the membrane quality could be minimized, doubly confirming the great potential of the YSZ additive for large-scale preparation of mullite hollow fibers.

Acknowledgements

This study was funded by the National Natural Science Foundation of China (22035002, 21776128, 21878147, and 21808106), National Key Research and Development Project (2018YFE0118200), the Leading Talent in Ten-Thousand Talent Program (2019), “333 Talent Project” of Jiangsu Province, the Young Fund of Jiangsu Province (BK20170132), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References

- [1] Liu S, Li K, Hughes R. Preparation of porous aluminium oxide (Al_2O_3) hollow fibre membranes by a combined phase-inversion and sintering method. *Ceram Int* 2003, **29**: 875–881.
- [2] Wei CC, Chen OY, Liu Y, *et al.* Ceramic asymmetric hollow fibre membranes—One step fabrication process. *J Membrane Sci* 2008, **320**: 191–197.
- [3] Lu H, Zhang L, Xing W, *et al.* Preparation of TiO_2 hollow fibers using poly(vinylidene fluoride) hollow fiber microfiltration membrane as a template. *Mater Chem Phys* 2005, **94**: 322–327.
- [4] Han L-F, Xu Z-L, Cao Y, *et al.* Preparation, characterization and permeation property of Al_2O_3 , Al_2O_3 - SiO_2 and Al_2O_3 -kaolin hollow fiber membranes. *J Membrane Sci* 2011, **372**: 154–164.
- [5] Xu G, Wang K, Zhong Z, *et al.* SiC nanofiber reinforced porous ceramic hollow fiber membranes. *J Mater Chem A* 2014, **2**: 5841–5846.
- [6] Kingsbury BFK, Li K. A morphological study of ceramic hollow fibre membranes. *J Membrane Sci* 2009, **328**: 134–140.
- [7] Wang B, Wu ZT, Livingston AG, *et al.* A novel phase transition technique for fabrication of mesopore sized ceramic membranes. *J Membrane Sci* 2009, **339**: 5–9.
- [8] Pereira D, Biasibetti GRS, Camerini RV, *et al.* Sintering of mullite by different methods. *Mater Manuf Process* 2014, **29**: 391–396.
- [9] Jung JS, Park HC, Stevens R. Mullite ceramics derived from coal fly ash. *J Mater Sci Lett* 2001, **20**: 1089–1091.
- [10] Dong YC, Lin B, Xie K, *et al.* Cost-effective macro-porous mullite-corundum ceramic membrane supports derived from the industrial grade powder. *J Alloys Compd* 2009, **477**: 350–356.
- [11] Lü Q, Dong X, Zhu Z, *et al.* Environment-oriented low-cost porous mullite ceramic membrane supports fabricated from coal gangue and bauxite. *J Hazard Mater* 2014, **273**: 136–145.
- [12] Zhu ZW, Wei ZL, Sun WP, *et al.* Cost-effective utilization of mineral-based raw materials for preparation of porous mullite ceramic membranes via *in situ* reaction method. *Appl Clay Sci* 2016, **120**: 135–141.
- [13] Fakhfakh S, Baklouti S, Baklouti S, *et al.* Elaboration and characterisation of low cost ceramic support membrane. *Adv Appl Ceram* 2013, **109**: 31–38.
- [14] Bakhtiari O, Samei M, Taghikarimi H, *et al.* Preparation and characterization of mullite tubular membranes. *Desalin Water Treat* 2011, **36**: 210–218.
- [15] Abdulhameed MA, Othman MHD, Joda HNAA, *et al.* Fabrication and characterization of affordable hydrophobic ceramic hollow fibre membrane for contacting processes. *J Adv Ceram* 2017, **6**: 330–340.
- [16] Zhu L, Dong YC, Li LL, *et al.* Coal fly ash industrial waste recycling for fabrication of mullite-whisker-structured porous ceramic membrane supports. *RSC Adv* 2015, **5**: 11163–11174.
- [17] Li LL, Chen ML, Dong YC, *et al.* A low-cost alumina-mullite composite hollow fiber ceramic membrane fabricated via phase-inversion and sintering method. *J Eur Ceram Soc* 2016, **36**: 2057–2066.
- [18] Yan S, Pan Y, Wang L, *et al.* Synthesis of low-cost porous ceramic microspheres from waste gangue for dye adsorption. *J Adv Ceram* 2017, **7**: 30–40.
- [19] Liu Y-F, Liu X-Q, Li G, *et al.* Low cost porous mullite-corundum ceramics by gelcasting. *J Mater Sci* 2001, **36**: 3687–3692.
- [20] Miao X. Porous mullite ceramics from natural topaz. *Mater Lett* 1999, **38**: 167–172.
- [21] Zhu L, Chen M, Dong Y, *et al.* A low-cost mullite-titania composite ceramic hollow fiber microfiltration membrane for highly efficient separation of oil-in-water emulsion. *Water Res* 2016, **90**: 277–285.
- [22] Dong Y, Zhou J-e, Lin B, *et al.* Reaction-sintered porous mineral-based mullite ceramic membrane supports made from recycled materials. *J Hazard Mater* 2009, **172**: 180–186.
- [23] Viswabaskaran V, Gnanam FD, Balasubramanian M. Effect of MgO , Y_2O_3 and boehmite additives on the sintering behaviour of mullite formed from kaolinite-reactive alumina. *J Mater Process Technol* 2003, **142**: 275–281.
- [24] Souto PM, Menezes RR, Kiminami RHGA. Sintering of commercial mulite powder: Effect of MgO dopant. *J Mater Process Technol* 2009, **209**: 548–553.
- [25] Chang QB, Yang YL, Zhang XZ, *et al.* Effect of particle

- size distribution of raw powders on pore size distribution and bending strength of Al_2O_3 microfiltration membrane supports. *J Eur Ceram Soc* 2014, **34**: 3819–3825.
- [26] Tan X, Liu S, Li K. Preparation and characterization of inorganic hollow fiber membranes. *J Membrane Sci* 2001, **188**: 87–95.
- [27] Shi Z, Zhang Y, Cai C, *et al.* Preparation and characterization of $\alpha\text{-Al}_2\text{O}_3$ hollow fiber membranes with four-channel configuration. *Ceram Int* 2015, **41**: 1333–1339.
- [28] Cai C, Zhang Y, Zhang C, *et al.* Microstructure modulation of $\alpha\text{-Al}_2\text{O}_3$ hollow fiber membranes with four-channel geometric configuration. *Asia-Pac J Chem Eng* 2016, **11**: 949–957.
- [29] Gao XC, Diniz da Costa JC, Bhatia SK. Understanding the diffusional tortuosity of porous materials: An effective medium theory perspective. *Chem Eng Sci* 2014, **110**: 55–71.
- [30] Bhatia SK. Capillary network models for transport in packed beds: Considerations of pore aspect ratio. *Chem Eng Commun* 1996, **154**: 183–202.
- [31] Friedman SP, Seaton NA. A corrected tortuosity factor for the network calculation of diffusion coefficients. *Chem Eng Sci* 1995, **50**: 897–900.
- [32] Li LS, Wang QF, Liao GH, *et al.* Densification behavior of mullite- Al_2TiO_5 composites by reaction sintering of natural andalusite and TiO_2 . *Ceram Int* 2018, **44**: 3981–3986.
- [33] Huang YX, Senos AMR, Baptista JL. Effect of excess SiO_2 on the reaction sintering of aluminium titanate–25vol% mullite composites. *Ceram Int* 1998, **24**: 223–228.
- [34] Yu H, Chen YJ, Guo XD, *et al.* Study on mechanical properties of hot pressing sintered mullite- ZrO_2 composites with finite element method. *Ceram Int* 2018, **44**: 7509–7514.
- [35] Kanno Y. Thermodynamic and crystallographic discussion of the formation and dissociation of zircon. *J Mater Sci* 1989, **24**: 2415–2420.
- [36] Mahnicka-Goremikina L, Svinka R, Svinka V. Influence of ZrO_2 and WO_3 doping additives on the thermal properties of porous mullite ceramics. *Ceram Int* 2018, **44**: 16873–16879.
- [37] Abd Aziz MH, Othman MHD, Hashim NA, *et al.* Fabrication and characterization of mullite ceramic hollow fiber membrane from natural occurring ball clay. *Appl Clay Sci* 2019, **177**: 51–62.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.