

低温烧结碳化硅陶瓷分离膜的制备及其油水分离性能

付锦绣¹, 翟凤瑞², 李 双¹

(1. 山东理工大学资源与环境工程学院, 山东 淄博 255049; 2. 红河学院, 云南 蒙自 661199)

摘 要: 碳化硅陶瓷分离膜具有高亲水性、耐化学腐蚀、抗膜污染等优异性能, 在大宗废水、强腐蚀废水、高温废水等的高效处理中受到广泛的关注。然而, 碳化硅是典型的强共价键化合物, 碳化硅陶瓷膜制备过程具有烧结温度高、制备能耗大等问题。本文采用优选的低熔点化合物作为烧结助剂, 经 1 000 °C 烧结制备了高强度、孔径均匀的碳化硅陶瓷分离膜。研究了烧结助剂含量对碳化硅陶瓷膜微观结构、孔径分布、相组成及油水分离性能等的影响。研究表明, 低熔点烧结助剂连接碳化硅颗粒形成陶瓷的骨架结构, 随着烧结助剂含量从 10%(质量分数)增加到 30%, 碳化硅陶瓷膜的孔隙率从 42%降低到 35%, 同时平均孔径从 3.5 μm 降低到 2.1 μm , 成孔模式由碳化硅颗粒堆积过渡到烧结助剂成孔。纯水实验表明, 烧结助剂含量为 30%时, 随着跨膜压差从 0.2 bar 增加到 0.5 bar 碳化硅陶瓷膜的分离通量从 120 L/(m²·h)增加到 306 L/(m²·h); 油水分离实验表明, 当跨膜压力差为 0.2 bar 时碳化硅陶瓷膜的截留率和分离通量分别为 93.3%和 123 L/(m²·h)。

关键词: 碳化硅; 气孔率; 陶瓷膜; 油水分离; 烧结助剂

中图分类号: TB332 文献标志码: A 文章编号: 0454-5648(2022)06-1572-10

网络出版时间: 2022-05-30



Low-Temperature Preparation of Silicon Carbide Ceramic Membrane for Oil-in-Water Separation

FU Jinxiu¹, ZHAI Fengrui², LI Shuang¹

(1. School of Resources and Environmental Engineering, Shandong University of Technology, Zibo 255049, Shandong, China;

2. Honghe University, Mengzi 661199, Yunnan, China)

Abstract: Silicon carbide ceramic membranes can be used in various water and wastewater treatments due to their high hydrophilicity, and superior chemical and thermal resistances. However, their applications are restricted due to some corresponding problems like high sintering temperature and then the high production cost. In this work, a low-temperature aid (LTA) bonded SiC ceramic symmetric membrane was sintered at 1 000 °C. The results show that LTA bonded SiC particles to form a skeleton of the symmetric membrane. The porosity of the membrane decreases from 42% to 35% and the average pore size decreases from 3.5 μm to 2.1 μm with the increase of LTA content from 10%(mass fraction) to 30%. Based on the results of the separation test on oil-in-water emulsion, the oil rejection and flow flux are 93.3% and 123 L/(m²·h) at the trans-membrane pressure of 0.2 bar, respectively. This study provides a low sintering temperature and energy saving strategy for the preparation of SiC ceramic membrane.

Keywords: silicon carbide; porosity; membrane; oil-water mixture; sintering aid

1 Introduction

Clean water is one of the most common and urgent resources in daily life. From the United Nations' 2030 goals for sustainable development, water shortage and the increasing demands for clean water have become a

worldwide concern^[1]. Thus, new effective, reliable and cost-effective technique is required for the separation and purification of various wastewaters so as to produce clean water^[2-3]. Among various water treatment processes, membrane filtration plays a great role due to its relative ease of operation and no chemical additives^[4-6]. Although

收稿日期: 2021-12-29. 修订日期: 2022-02-16.

基金项目: 山东省自然科学基金(ZR2020MEM027 和 ZR2020MEM026)资助。

第一作者: 付锦绣(1997—), 女, 硕士研究生。

通信作者: 李 双(1981—), 男, 博士, 副教授。

Received date: 2021-12-29. Revised date: 2022-02-16.

First author: FU Jinxiu(1997—), female, Master candidate.

E-mail: Fujinxiu2021@163.com

Correspondent author: LI Shuang(1981—), male, Ph.D., Associated Professor.

E-mail: lishuang@sdu.edu.cn

various kinds of membrane materials have been developed and utilized, ceramic membranes are gaining more and more attentions in various applications, such as petrochemical engineering, gas separation and food processing, due to their superior fouling resistance, better hydrophilicity, high permeability, and remarkable chemical/thermal stability^[7–10].

The majority of existing commercial ceramic membranes are oxides, such as alumina^[11], zirconia^[12], mullite^[13] and silica^[14]. Silicon carbide ceramic membrane is popular as one of the most promising inorganic materials for water treatment. From the literatures, silicon carbide membrane exhibits a great water permeability because of the high surface hydrophilicity^[15], and excellent fouling resistance because of the negative charge on material surface^[1, 16].

However, there are still some challenges for the commercialization of silicon carbide membrane. One is the high-energy consumption and specific sintering furnace for the sintering of SiC membrane. As a result of the strong covalent bonds (Si—C), the sintering temperature of SiC ceramics is usually as high as 2 000 °C, thus leading to a greater energy consumption in sintering (*i.e.*, 60% of the full production cost)^[17]. In our

previous studies on the evaporation-condensation derived SiC membrane^[18–19], the substrate was firstly sintered at 2 200 °C and then the selective layer was sintered at 1 900 °C. Although such a sintered membrane has an excellent resistance to strong acid and alkali, this sintering procedure at high temperatures is a high-energy consumption and long period process. Also, the intrinsic brittleness of the membrane is another challenge, thereby causing the brittle fracture of SiC ceramics and having some difficulties in the transportation and installation of SiC membranes^[20]. As a result, the full-scale application of SiC ceramic membranes is still restricted due to the high production cost and poor mechanical properties (*i.e.*, the intrinsic brittleness).

To address the issues above, some corresponding studies have been carried out to prepare SiC ceramic membrane at low temperature^[21–23]. Table 1 summarizes the preparation parameters and structures of SiC porous membranes sintered with different low-temperature sintering aids. Clearly, the densification temperature of SiC membrane sintered in the presence of low-temperature aids significantly decreases, compared with that of SiC membrane sintered in the absence of low-temperature aids.

Table 1 Preparation parameters and structures of SiC porous membranes sintered with different low-temperature aids

Low-temperature aid	w(low-temperature aid)/%	Temperature/°C	Sintering Time/h	Porosity/%	Strength/MPa	APS/μm	Reference
Bentonite powders	N/A	1 400	2	39.5	48.6±3.1	N/A	[24]
Water glass	4–14	600–1 100	2	39–47	56–83	0.58–0.75	[25]
Mullite fibers	4	1 450	4	47	15.7	20	[26]
bauxite	30	1 400	3	45–59	41–17	6.1	[27]
Glass frit	15	850	2	37–46	75	3.3	[28]
NaA zeolite	8	1 200	4	51.2	25	16.2	[29]
Fly ash	20	1 400	3	34.9	N/A	N/A	[30]
Clay	48	1 400	1	47.5	47.5	1.8	[31]
Al ₂ O ₃ –Y ₂ O ₃	4	1 500–1 800	2	42	15–56	N/A	[32]
Mullite	10	1 400	3	36.8	22.5	N/A	[33]

w—Mass fraction.

In general, high-purity oxide powders are utilized as a low-temperature sintering aid to accelerate the densification and consequently enhance the mechanical strength of ceramic bulks. Fukushima *et al.*^[32] fabricated a porous SiC membrane support with Al₂O₃–Y₂O₃ additives, and small grains and fine pores with the sizes of 200–300 nm were detected. The results showed that the grain size and pore size of the ceramic support both increased with increasing the sintering temperature (*i.e.*, 1 500–1 800 °C) at the additive fraction of 1.0%. Han *et al.*^[26] chose high-purity zirconia and mullite fiber as additives for the sintering of SiC membrane. It was found that the trade-off effect between porosity and strength was offset for the introduction of mullite fiber. Moreover, the porosity and bending strength increased to 46.8% and 15.7 MPa, respectively, when the SiC membrane was sintered at 1 450 °C for 4 h.

To further decrease the sintering temperature of SiC ceramics, some studies focused on some low-temperature and low-cost materials, such as clay, fly ash, kaolin, apatite, *etc.*^[6, 34–36]. For instance, using a recycled NaA residue as sintering additives, Yang *et al.*^[29] prepared a highly stable porous SiC membrane, where an addition of 8% of NaA residue could decrease the sintering temperature of SiC membrane from 2 000 to 1 200 °C. Recently, the high-value added utilization of fly ash has gained increasing attentions. From the work by Liang *et al.*^[30], fly ash was transformed into mullite with needle-shaped at 1 300 °C, leading to a porous structure with micropores and windows in SiC porous ceramics. The introduction of fly ash increased the contact angle between ceramic substrate and molten metal, thus favoring the filtration of high-temperature wastewater. Clearly, these low-cost additives could reduce the

sintering temperature and enhance the mechanical properties of SiC ceramic membranes. However, the composition of these additives depends on the manufacturers or production sites, thus affecting the fabrication parameters and permeation-selectivity properties of SiC membranes.

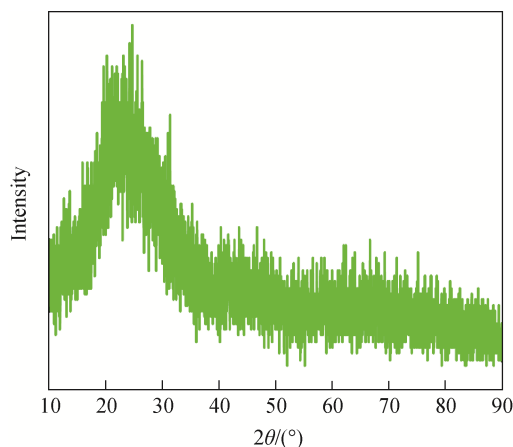
In this paper, a silicon carbide ceramic membrane was fabricated at a low temperature to reduce the energy consumption during sintering and accelerate the full-scale application of SiC ceramic membrane. A low-temperature glaze was chosen as sintering aid (low-temperature aid, LTA). The effect of LTA content on the morphology, phase composition and pore size of the membranes was elaborated. In addition, the evolution of pore size at various LTA contents and then the water flux and selectivity of the membrane were discussed. Microfiltration is becoming an emerging and promising separation strategy for the pre-treatment of oily wastewater because of its high separation efficiency, long serving life-time and ease of operation. Thus, the filtration performance of LTA bonded SiC symmetric membrane in the separation of oil-in-water emulsion was also investigated.

2 Experimental

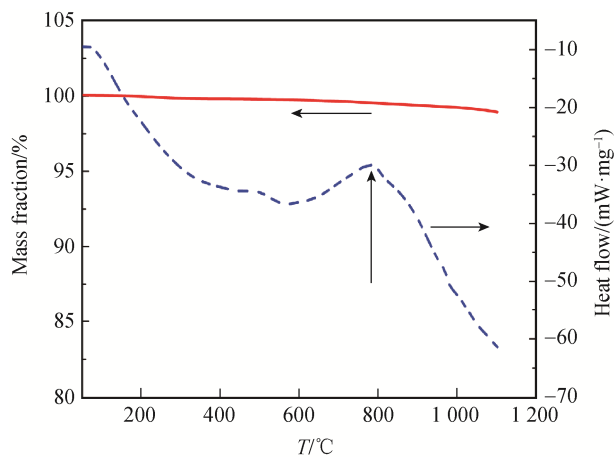
2.1 Starting materials

Silicon carbide particles (SiC, 99%(mass fraction) Shantian Co., Ltd, Linshu, China) with an average size of 10 μm , and low-temperature aid (LTA, Foshan Top Glaze Co., Ltd, Foshan, China) were used as the starting materials. To improve the plasticity of the green body and the dispersion of silicon carbide particles, sodium carboxymethyl cellulose (CMC) and polyacrylic acid (PAA) were used as additives.

Fig. 1 shows the particle size distribution and microstructure of SiC particles as raw materials. Clearly, the commercial SiC particles present uniform structures with average particle sizes of approximately 10 μm . Such a microstructure favors the formation of uniform and interconnected pores in the membrane.



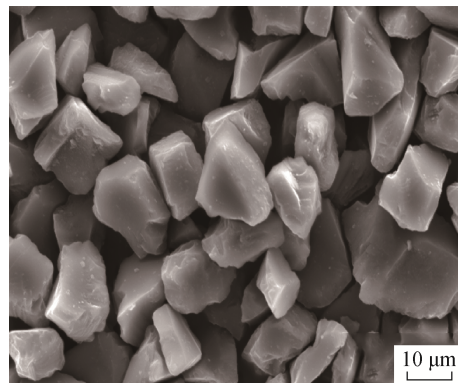
(a) XRD pattern



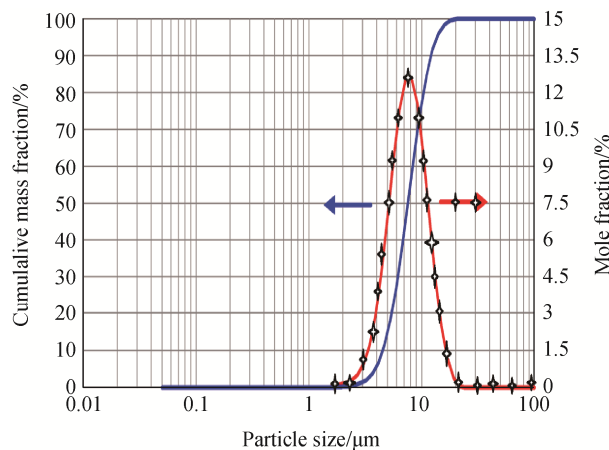
(b) TG-DSC curves

Fig. 2 Composition and thermal properties of the low-temperature aid

Fig. 2 shows the X-ray diffraction (XRD) patterns and thermogravimetry-differential thermal analysis (TG-DTA) curves of LTA. In Fig. 2(a), LTA is composed of amorphous phase, which is a low-temperature frit in fact. As the frit was prepared by rapid cooling of glassy phase from high temperature, it did not have enough chance to crystallize. Although this, a significant peak occurred at 20°–30°, which corresponds to the mixture of



(a) SEM photograph



(b) Particle size distribution

Fig. 1 Characteristics of the starting SiC particles

Na_2SiO_3 and $\text{Al}_2(\text{SiO}_3)_3$. In Fig. 2(b), there is little mass change in the temperature range from ambient temperature to 1 200 °C; an exothermic peak occurred at approximately 800 °C, corresponding to the melting point of LTA. Based on this, the LTA bonded silicon carbide membrane can be sintered at approximately 800 °C. Table 2 shows the element composition of LTA determined by X-ray fluorescence spectrometry (XRF). Clearly, the LTA mainly consists of SiO_2 , Na_2O and Al_2O_3 . The element distribution of LTA in the silicon carbide membrane will be discussed in the next section.

Table 2 Element composition of low-temperature aid

Oxide	SiO_2	Na_2O	Al_2O_3	BaO	CaO	Others
w/%	64.2	8.44	8.07	4.09	3.49	11.71

2.2 Specimen preparation

To prepare a batch of LTA bonded silicon carbide membranes, SiC particles, LTA, CMC and PAA were weighed precisely and then wet mixed in a planetary ball mill with SiC balls as grinding media for 24 h. The mixture was dried, sieved and uniaxially pressured at 20 MPa for soaking time of 20 s. After drying in air, the green body was sintered at 1 000 °C for 120 min. To avoid the formation of cracks in the green body, a low heating rate of 3 °C/min was used during heating. In this study, three specimens with different mass contents of LTA (*i.e.*, 10%, 20% and 30%), respectively, were prepared. In addition, the mass contents of CMC and PAA were 2% and 0.5%, respectively. The specimens have the symmetric structures as symmetric membrane.

2.3 Characterization

Morphologies of the starting particles and the sintered ceramic membranes were observed by a model LEO-1 503 scanning electron microscopy (SEM, LEO Co., Oberkochen, Germany). The element composition of the as-purchased LTA was determined by a model ZSC100e X-ray fluorescence spectrometer (XRF, Rigaku Co., Ltd., Tokyo, Japan). The thermal properties of LTA were investigated by a model Q100 thermogravimetry-differential thermal analyser (TG-DSC, TA Co., Ltd., New Castle, USA). The phase compositions of the specimens were measured by a model D/max 2 550HB X-ray diffractometer (XRD, Rigaku Co., Ltd., Tokyo, Japan). The porosity of the ceramic membrane was measured by the Archimedes method. The pore size distribution of the membranes was investigated by a mercury intrusion method on a model AutoPore IV 9 510 instrument (Microtrac Co., Ltd., Norcross, USA).

The pure-water flux of the membranes was characterized by a self-made equipment. The ceramic membranes with the diameter of 50 mm and the thickness of 5 mm were used. The water flux J was calculated by the following equation:

$$J = \frac{V}{A \times \Delta t} \quad (1)$$

where V is the volume of permeate (L); A is the effective membrane area (m^2); Δt is the sampling time (h).

To investigate oil-in-water separation performances of SiC ceramic membranes, five oil-in-water emulsions were prepared at different concentrations (*i.e.*, 2 001 g/L). The diesel oil was dissolved into 500 mL deionized water with the addition of 0.5 g sodium dodecyl benzene sulfonate (SDBS, Aladdin Industrial Co., Shanghai, China) as a surfactant, and dispersed in a high-speed stirrer at a rotational speed of 5 000 r/min for 30 min. Finally, the oil-water mixture was further dispersed *via* vigorous magnetic stirring for approximately 24 h, until it presented high stability and homogeneity.

Fig. 3 shows the size distribution of oil drops in the oil-in-water emulsion. In Fig. 3, oil drops in the emulsion are distributed in a size range of 5–10 μm . The oil concentration in the permeate emulsion was determined by a model UV-5 100B UV-visible spectrometer (Metas Co., Shanghai, China). The oil rejection (R) of the membranes was calculated by

$$R = (1 - \frac{C_p}{C}) \times 100\% \quad (2)$$

where C and C_p are the concentrations of oil in the feed and the permeate (mg/L), respectively.

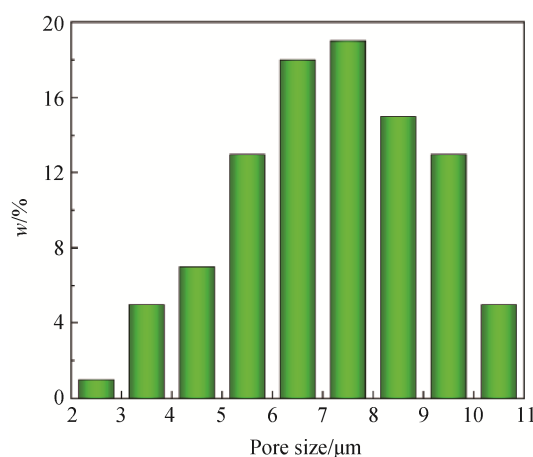


Fig. 3 Size distribution of oil drops in the oil-in-water emulsion

3 Results and discussion

3.1 Microstructure and composition of LTA bonded SiC membrane

As an ideal membrane material, ceramic membrane should have a high fracture strength to withstand trans-membrane pressure and backwash, and the high porosity and suitable pore size are beneficial to the permeability and selectivity of the ceramic membrane. Fig. 4 shows the microstructures of LTA bonded SiC membrane sintered at 1 000 °C and different LTA contents. In Figs. 4(a)–4(c), SiC particles are bonded tightly to form a skeleton of the membrane, and the number and size of the open pores decrease with the increase of LTA content. In Fig. 4(d), LTA has bonded the SiC particles together,

which is achieved by the spreading of the liquid phase on the particle surface at a high temperature. The bonding strength between SiC particles is low at a low LTA content (*i.e.*, 10%), and the resultant pores are mainly inter-particle

pores. In Figs. 4(e) and 4(f), LTA produces a thicker boundary between the coarse particles and then smaller pores. This indicates that the pore size and thickness of the boundaries can be adjusted by the LTA content.

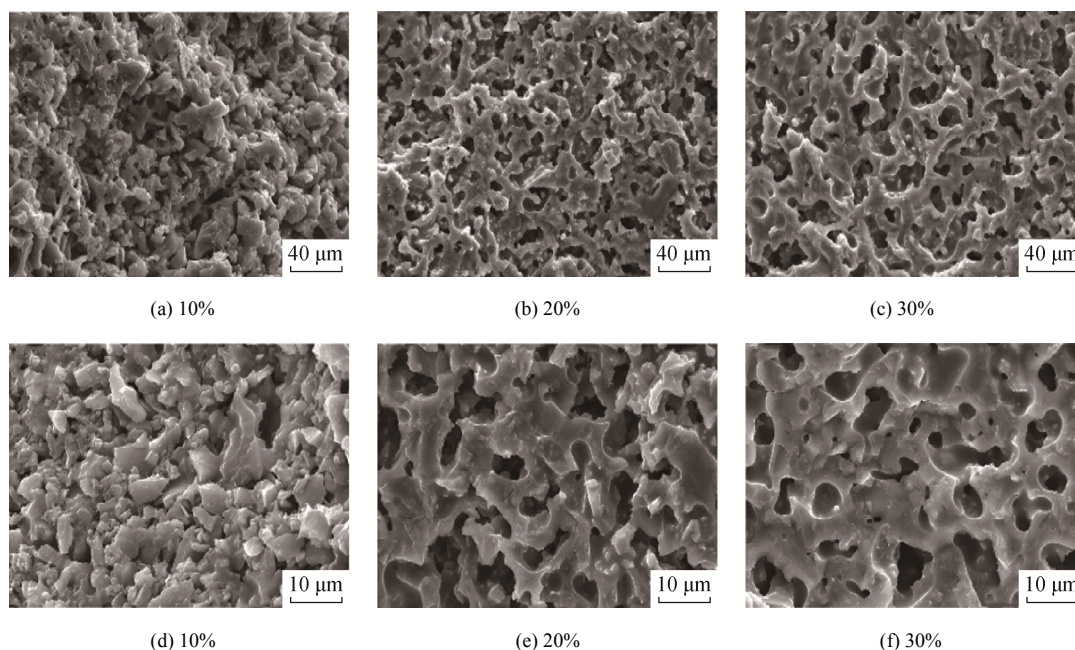


Fig. 4 SEM micrographs of LTA bonded SiC membrane sintered at 1000 °C and different LTA contents

According to the microstructure and thermal analysis, the microstructure evolution of LTA bonded SiC membrane can be illustrated in Fig. 5. (a) The starting SiC and LTA particles were bonded by CMC to form green body; (b) When heated to 600 °C, the organic matters such as CMC and PAA were pyrolyzed; (c) At 800 °C, the LTA started to melt and infiltrate the green body; (d) molten LTA bonded SiC particles and two types of pores. At the lower LTA content, the majority of pores derive from the packing of SiC particles, thus leading to the large pore size, while at the higher LTA content, some smaller pores form because of the infiltration of LTA.

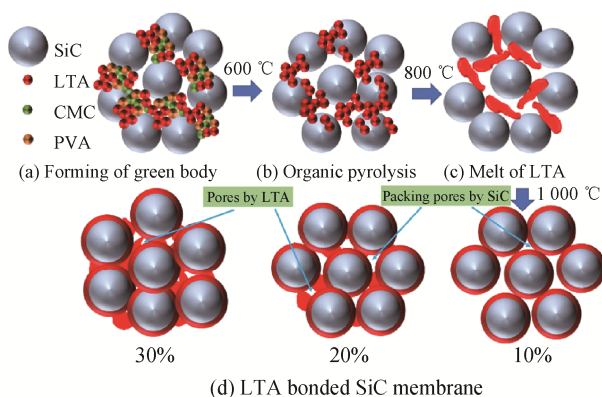


Fig. 5 Microstructure evolution of LTA bonded SiC membrane during sintering

Fig. 6 shows the element distribution of SiC membrane with LTA content of 20%. In Fig. 6(a), SiC

particles are bonded strongly by LTA to form a sintered body with high fracture strength. Thus, a homogeneous distribution of LTA is important. In Fig. 6(b), elements O, Al and Na from LTA distribute uniformly around SiC particles.

According to the microstructure and element distribution analysis, the sintering mechanisms of LTA bonded silicon carbide membrane are as follows: at a low melting temperature, LTA is transformed into a viscous phase at a low temperature, and then SiC particles are immersed and wrapped and some pores between SiC particles are infiltrated and filled. After cooling, as-formed glassy LTA bonds with SiC particles, resulting in a sintered body with high strength and porous structure.

Fig. 7 shows the XRD patterns of the ceramic membrane sintered at 1000 °C and different LTA contents. Clearly, all the specimens consist of a plenty of SiC and a trace of Na_2SiO_3 and $\text{Al}_2(\text{SiO}_3)_3$. The most of LTA is amorphous phase, which cannot be detected by XRD analysis. When the specimens are heated at 1000 °C for 120 min, some Na_2SiO_3 and $\text{Al}_2(\text{SiO}_3)_3$ phases crystallize from the liquid phases, corresponding to the typical peaks in the XRD patterns. This is different from the patterns of the starting LTA, as shown in Fig. 2(a), where only a wide diffusion peak occurs between 20° and 30°. Moreover, a cristobalite phase, which is usually produced by the oxidation reaction between SiC and O_2 at a high temperature is not detected. This may be due to the isolate effect of glassy phase at high temperature, which prevents the oxidation reaction between SiC and O_2 .

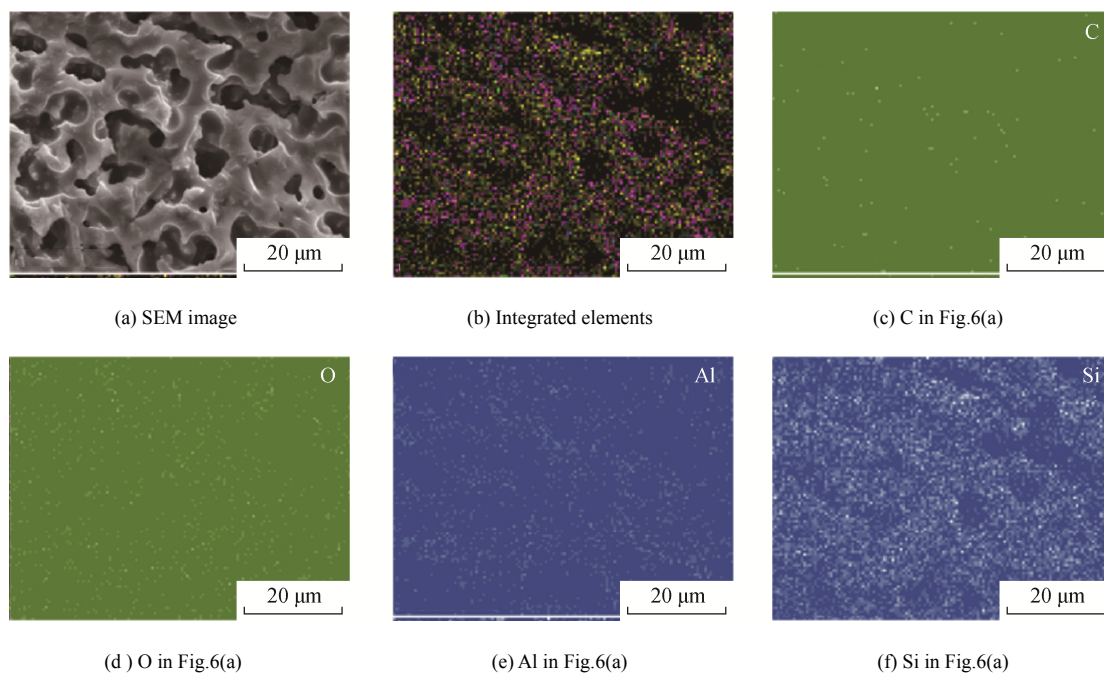


Fig. 6 Element distribution of the ceramic membrane at LTA contents of 20%

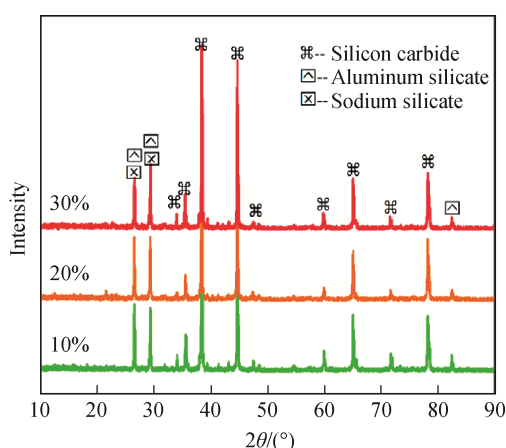


Fig. 7 XRD patterns of the ceramic membrane sintered at 1000 °C and different LTA contents

3.2 Pore structures and permeability of the LTA bonded SiC membrane

Fig. 8 shows the effect of LTA content on the bulk density and porosity of ceramic membrane. The bulk density of the ceramic membrane was measured by Archimedes method. Clearly, the bulk density of the membrane decreases from 1.74 g/cm³ to 1.59 g/cm³, and the porosity decreases from 42% to 35% as the LTA content increases from 10% to 30%. The variation of porosity can be ascribed to the difference in packing density of the starting particles and degree of particles sintering. The packing density of the green body increases with the increase of LTA content because of the small size of LTA. Besides, the particles densification of SiC ceramic membrane is accelerated by the viscous flow of LTA during sintering: a high fraction of viscous flow enhances the densification of the particles. Although the

enhanced densification, the bulk density of the ceramic membrane decreases with the increase of LTA content due to density difference between SiC and LTA: the density of LTA is much smaller than that of SiC.

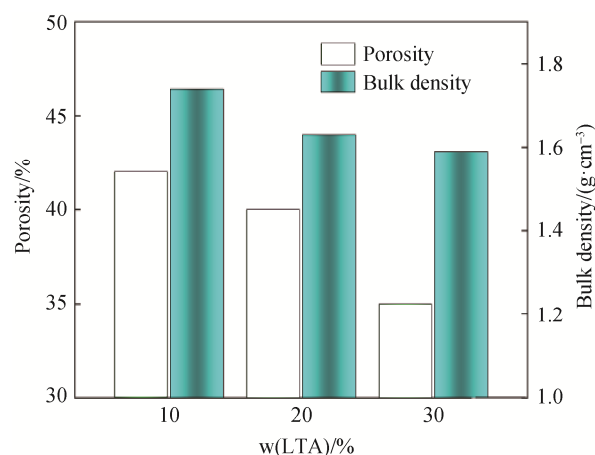


Fig. 8 Porosity and bulk density of the ceramic membrane with different LTA contents

The size and distribution of pores are the major factors in determining the permeability and selectivity of ceramic membrane. Fig. 9 shows the pore size distribution of LTA bonded SiC membrane by mercury intrusion method. The average pore size of the membrane decreases from 3.5 μm to 2.1 μm with the increase of LTA content from 10% to 30%, resulting from the increase in the thickness of grain boundaries between SiC particles. Also, the volume fraction of pores decreases with the increase of LTA content, which agrees well with the changing trends of porosity (see Fig. 8). Fig. 10 shows the formation mechanism of pores in LTA bonded SiC

ceramics. For the specimen with 10% LTA content, the pores mainly stem from the packing of the starting SiC particles, and only a small amount of the open pores form due to the LTA phase, as marked by the green circles in Fig. 10(a). With the increase of sintering aid, the molten LTA filtrates into the space between SiC particles, and the thickness of the grain boundaries declines. As a result, the more pores form due to the LTA phase (see Fig. 10(b)). In addition, the addition of CMC and PAA also

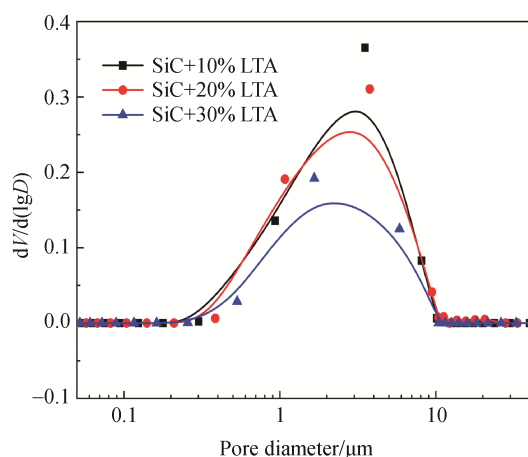
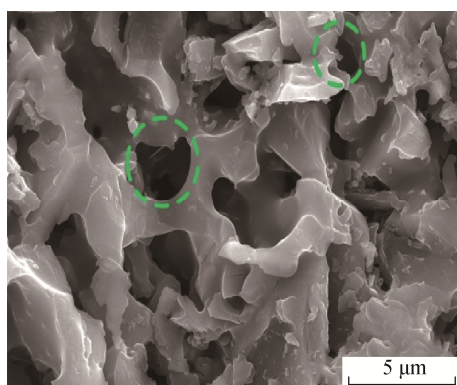
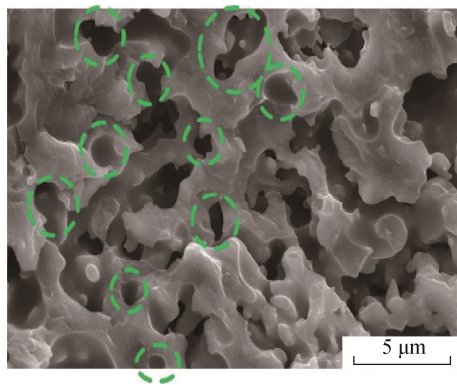


Fig. 9 Pore size distributions of the ceramic membranes at different LTA contents



(a) 10%



(b) 30%

Fig. 10 Mechanism of pore formation in LTA bonded SiC ceramics

affects the structure of pores: PAA enhances the dispersion of SiC particles, consequently improving the uniformity of the pores, and CMC increases the pore size and porosity of the membrane after pyrolysis and carbonization.

Fig. 11 shows the water flux of LTA bonded SiC membranes as a function of trans-membrane pressure (0–0.5 bar). Clearly, the water flux of three membranes increased linearly with the increase of trans-membrane pressure, which follows Darcy's law. Thus, the permeation of pure water across all LTA bonded SiC membrane follows the viscous flow model. For the specimen with LTA content of 10%, the water flux increases from 142 L/(m²·h) to 358 L/(m²·h) with increasing the trans-membrane pressure from 0.2 bar to 0.5 bar. The water flux of the specimen with 30% LTA content increases from 120 L/(m²·h) to 306 L/(m²·h) as the trans-membrane pressure increases from 0.2 bar to 0.5 bar because of the decreased porosity and average pore size.

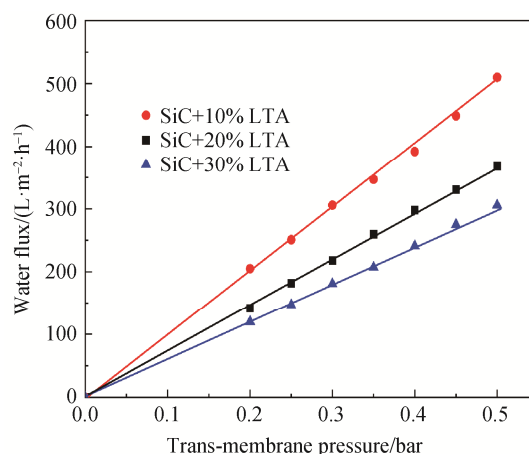


Fig. 11 Water flux of LTA bonded SiC membranes as a function of trans-membrane pressure

High-efficient separation of oil-water mixture is a challenge in various industrial and agricultural fields. Thus, the permeability and selectivity of LTA bonded SiC membrane were investigated *via* oil-in-water emulsion. In this study, the size of the oil drops was distributed in the range from 5 μm to 10 μm and five emulsions with different concentrations (*i.e.*, 200–1 000 mg/L) were prepared.

Fig. 12 shows the microstructures of the oil-in-water emulsion with the concentration of 1 000 mg/L before and after filtration. After the dead-end microfiltration process at the trans-membrane pressure of 0.2 bar, most of the oil drops are removed from the oil-in-water emulsion (see in Figs. 12(a) and 12(b)), indicating a superior separation performance for the oil-in-water emulsion. In Fig. 12(c), the oil rejection increases from 89.1% to 92.5% with the increase of LTA content from 10% to 30%, ascribing to the decline in the porosity and average pore size of the ceramic membrane. In addition, Fig. 12(d) also shows the separation performance of LTA bonded SiC membrane.

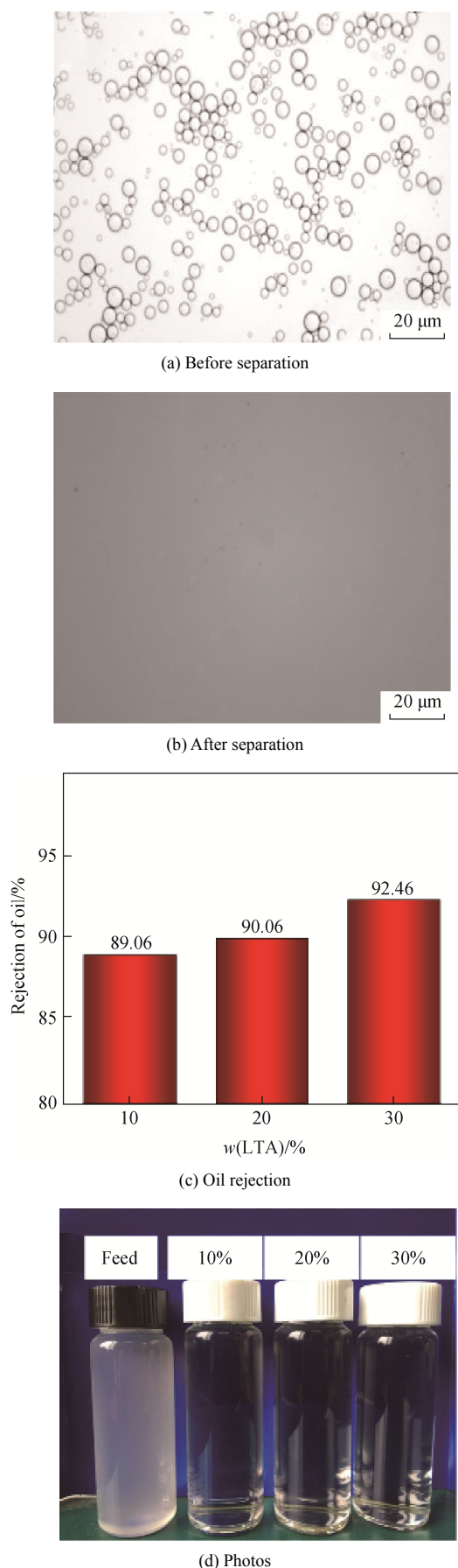


Fig. 12 Filtration performances of the membrane on oil-water wastewater

Fig. 13 shows the oil rejection of the ceramic membrane with different LTA contents at the trans-membrane pressure of 0.2 bar. Clearly, at a trans-membrane pressure of 0.2 bar, the rejection rate increases with the increase of emulsion concentration. For the specimen with 10% LTA content, the rejection rate increases from 89.1% to 89.3% due to the decreased porosity and average pore size. The rejection rate increases from 92.5% to 94.3% for the specimen with 30% LTA content. The large pore channels are blocked by the fine particles when the high-concentration emulsion passes the membrane, thus preventing the penetration of large particles. Also, the oil particles can easily get into the cake layer on the membrane surface, which prevents the penetration of large particles. It is thus indicated that the selectivity of SiC membrane can be adjusted by an appropriate LTA content.

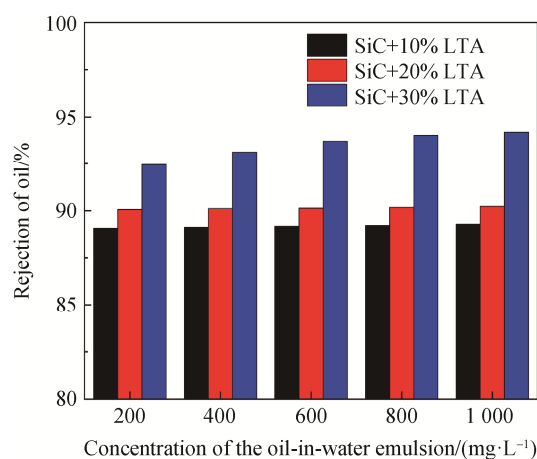


Fig. 13 Oil rejection of the ceramic membrane with different LTA contents at the trans-membrane pressure of 0.2 bar

To enhance separation efficiency of ceramic membrane, high trans-membrane pressure is usually applied, thus the variations of rejection rate and flowing flux of the ceramic membrane with the increase of trans-membrane pressure are presented in Fig. 14. For the ceramic membrane with 30% LTA content, the oil rejection decreases slowly with the increase of trans-membrane pressure from 0.1 bar to 0.4 bar. In Fig. 14a, a decreased oil rejection occurs at a trans-membrane pressure of approximately 0.3 bar. The average pore size of the ceramic membrane used is 2.5 μm . It is believed that such a trans-membrane pressure favors the penetration of large particles. For the emulsion with concentration of 200 mg/L, the rejection rate decreases from 93.3% to 87.2% with the increase of trans-membrane pressure from 0.1 bar to 0.4 bar, while the rejection rate decreases from 95.1% to 90.1% for the emulsion with concentration of 1000 mg/L. Thus, the low concentration emulsion can be more effectively treated at a lower trans-membrane pressure.

In Fig. 14(b), the flow flux of the ceramic membrane increases with the increase of trans-membrane

pressure because of the “trade-off” effect. For the low concentration emulsion (*i.e.*, 200 mg/L), the flow flux increases from 123 L/(m²·h) to 380 L/(m²·h) with the increase of trans-membrane pressure from 0.1 bar to 0.4 bar, while the flow flux increases only from 29 L/(m²·h) to 98 L/(m²·h) at the emulsion concentration of 1 000 mg/L. Xing et al. [20] also investigated the separation performance of low-temperature sintered SiC ceramic membrane on oil-in-water mixtures when sintering the ceramic membrane at 1 000 °C with zeolite residue as the sintering aid. The ceramic membrane presented oil contact angle of 173.4°±0.5°, thus a high rejection rate (>90%) in various oil-in-water emulsions at the average pore size of 0.4 μm. Therefore, low-temperature sintered SiC membrane can be used in the efficient separation of large-scale oil-in-water mixtures.

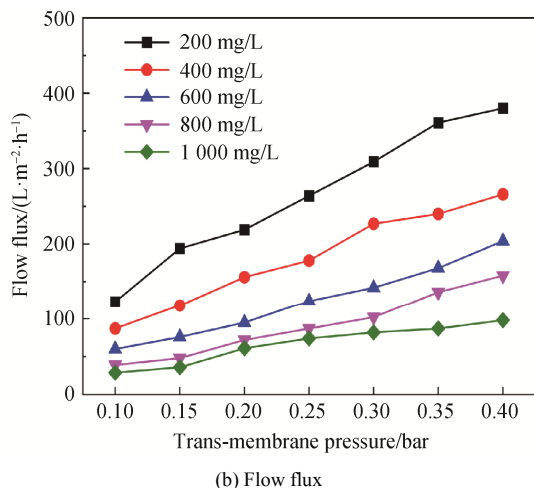
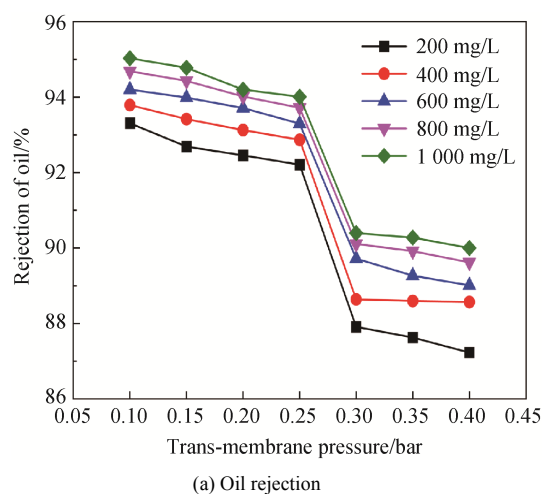


Fig. 14 Filtration behaviors of the ceramic membrane with LTA content of 30%

4 Conclusions

A silicon carbide symmetric membrane was prepared with SiC particles of 10 μm as the skeleton phase and low-temperature aid as the bonding phase. The symmetric membrane was sintered in a muffle furnace at 1 000 °C, which was an extremely low temperature for

the fabrication of SiC ceramic membrane. The effects of LTA mass on the microstructure, phase composition, pore size and then the corresponding permeation and separation properties of LTA bonded SiC membrane were investigated.

In LTA bonded SiC membrane, the SiC particles were bonded tightly by LTA to form skeleton of the membrane. During sintering, LTA transformed into a viscous substance, and then infiltrated and filled the packed bodies, resulting in sintered body with high strength and porous structure after cooling. The results indicated that both the number and size of the open pores decreased with the increase of LTA content from 10% to 30%.

For the permeability and selectivity properties, the porosity of the membrane decreased from 42% to 35% and the average pore size decreased from 3.5 μm to 2.1 μm with the increase of LTA content from 10% to 30%. The pure water flux was investigated to characterize the permeability of the membrane. The permeability increased linearly with the increase of trans-membrane pressure, which could be adjusted by changing LTA content. Based on the results of separation test on oil-in-water emulsion, the oil rejection and flow flux were 93.3% and 123 L/(m²·h) at the trans-membrane pressure of 0.2 bar, respectively.

References:

- [1] ERAY E, CANDELARIO V M, BOFFA V, et al. A roadmap for the development and applications of silicon carbide membranes for liquid filtration: Recent advancements, challenges, and perspectives[J]. Chem Eng J, 2021, 414: 128826.
- [2] AHMAD N A, GOH P S, YOGARATHINAM L T, et al. Current advances in membrane technologies for produced water desalination[J]. Desalination, 2020, 493: 114643.
- [3] AHMAD T, GURIA C, MANDAL A. A review of oily wastewater treatment using ultrafiltration membrane: A parametric study to enhance the membrane performance[J]. J Water Process Eng, 2020, 36: 101289.
- [4] BERNARDO P, IULIANELLI A, MACEDONIO F, et al. Membrane technologies for space engineering[J]. J Membrane Sci, 2021, 626: 119177.
- [5] PADAKI M, MURALI R S, ABDULLAH M S, et al. Membrane technology enhancement in oil–water separation. A review[J]. Desalination, 2015, 357: 197–207.
- [6] HE Zeming, LYU Z Y, GU Qilin, et al. Ceramic-based membranes for water and wastewater treatment[J]. Colloid Surface A, 2019, 578: 123513.
- [7] GOH P S, ISMAIL A F. A review on inorganic membranes for desalination and wastewater treatment[J]. Desalination, 2018, 434: 60–80.
- [8] YU Ji, YU Sunjun, QI Hong. Effect of Alumina Doping on Properties of Macroporous Silicon Carbide Supports[J]. J Chin Ceram Soc, 2017, 45(12): 1810–1817.
- [9] MEULENBERG W A, SCHULZE F, DEIBERT W, et al. Ceramic membranes: materials-components-potential applications[J]. Chembioeng Rev, 2019, 6(6): 198–208.
- [10] HAMMEL E C, IGHODARO O L R, OKOLI O I. Processing and

- properties of advanced porous ceramics: An application based review[J]. *Ceram Int*, 2014, 40(10): 15351–15370.
- [11] ZHU Zhiwen, XIAO Jin, HE Wei, et al. A phase-inversion casting process for preparation of tubular porous alumina ceramic membranes[J]. *J Eur Ceram Soc*, 2015, 35(11): 3187–3194.
- [12] SHI Yanuo, FLURI A, GARBAYO I, et al. Zigzag or spiral-shaped nanostructures improve mechanical stability in yttria-stabilized zirconia membranes for micro-energy conversion devices[J]. *Nano Energy*, 2019, 59: 674–682.
- [13] CHEN Mingliang, ZHU Li, DONG Yingchao, et al. Waste-to-resource strategy to fabricate highly porous whisker-structured mullite ceramic membrane for simulated oil-in-water emulsion wastewater treatment[J]. *ACS Sustain Chem Eng*, 2016, 4(4): 2098–2106.
- [14] SHENG Huiying, KIM Y W, SONG I H. Processing of silicon-derived silica-bonded silicon carbide membrane supports[J]. *Ceram Int*, 2019, 45(2): 2161–2169.
- [15] LUO Lulei, CHEN Xuelong, WANG Yue, et al. Bio-inspired modification of silicon carbide foams for oil/water separation and rapid power-free absorption towards highly viscous oils[J]. *Ceram Int*, 2018, 44(11): 12021–12029.
- [16] LI Chen, SUN Wenjun, LU Zedong, et al. Ceramic nanocomposite membranes and membrane fouling: A review[J]. *Water Res*, 2020, 175: 115674.
- [17] ZOU Dong, FAN Yiqun. State-of-the-art developments in fabricating ceramic membranes with low energy consumption[J]. *Ceram Int*, 2021, 47(11): 14966–14987.
- [18] LI Shuang, WEI Chunheng, ZHOU Lijuan, et al. Evaporation-condensation derived silicon carbide membrane from silicon carbide particles with different sizes[J]. *J Eur Ceram Soc*, 2019, 39(5): 1781–1787.
- [19] LI Shuang, WEI Chunheng, ZHOU Lijuan, et al. Tuning microstructures and separation behaviors of pure silicon carbide membranes[J]. *Ceram Int*, 2019, 45(15): 18788–18794.
- [20] JIANG Qian, ZHOU Jian, MIAO Yu, et al. Lower-temperature preparation of SiC ceramic membrane using zeolite residue as sintering aid for oil-in-water separation[J]. *J Membrane Sci*, 2020, 610: 118238.
- [21] GOU Mintao, HUANG Jianguo. Preparation of Low-cost Porous Silicon Carbide Ceramic Support for Optimized Acid and Alkali Corrosion Resistance[J]. *J Chin Ceram Soc*, 2019, 47(12): 1737–1745.
- [22] CIORA R J, FAYYAZ B, LIU P K T, et al. Preparation and reactive applications of nanoporous silicon carbide membranes[J]. *Chem Eng Sci*, 2004, 59(22-23): 4957–4965.
- [23] VOIGT I, RICHTER H, STAHN M, et al. Scale-up of ceramic nanofiltration membranes to meet large scale applications[J]. *Sep Purif Technol*, 2019, 215: 329–334.
- [24] YUAN Bo, LI Hongxia, WANG Gang, et al. Preparation and properties of porous silicon carbide based ceramic filter[J]. *J Alloy Compd*, 2016, 684: 613–615.
- [25] JIANG Qian, XIE Yuling, JI Lingqian, et al. Low-temperature sintering of a porous SiC ceramic filter using water glass and zirconia as sintering aids[J]. *Ceram Int*, 2021, 47(18): 26125–26133.
- [26] HAN Feng, ZHONG Zhaoxiang, YANG Yi, et al. High gas permeability of SiC porous ceramics reinforced by mullite fibers[J]. *J Eur Ceram Soc*, 2016, 36(16): 3909–3917.
- [27] BAI Chengying, LI Yu, LIU Zhangmin, et al. Fabrication and properties of mullite-bonded porous SiC membrane supports using bauxite as aluminum source[J]. *Ceram Int*, 2015, 41(3): 4391–4400.
- [28] KIM S C, KIM Y W, SONG I H. Processing and properties of glass-bonded silicon carbide membrane supports[J]. *J Eur Ceram Soc*, 2017, 37(4): 1225–1232.
- [29] YANG Yi, XU Wenqi, ZHANG Feng, et al. Preparation of highly stable porous SiC membrane supports with enhanced air purification performance by recycling NaA zeolite residue[J]. *J Membrane Sci*, 2017, 541: 500–509.
- [30] LIANG Xiong, LI Yawei, YAN Wen, et al. Preparation of SiC reticulated porous ceramics with high strength and increased efficient filtration via fly ash addition[J]. *J Eur Ceram Soc*, 2021, 41(4): 2290–2296.
- [31] BUKHARI S Z A, HA J H, LEE J, et al. Fabrication and optimization of a clay-bonded SiC flat tubular membrane support for microfiltration applications[J]. *Ceram Int*, 2017, 43(10): 7736–7742.
- [32] FUKUSHIMA M, ZHOU Y, YOSHIZAWA Y. Fabrication and microstructural characterization of porous SiC membrane supports with Al_2O_3 - Y_2O_3 additives[J]. *J Membrane Sci*, 2009, 339(1-2): 78–84.
- [33] LUO Zhiyong, HAN Wei, LIU Kaiqi, et al. Influence of bonding phases on properties of *in-situ* bonded porous SiC membrane supports[J]. *Ceram Int*, 2020, 46(7): 8536–8542.
- [34] ZOU Dong, QIU Minghui, CHEN Xianfu, et al. One step co-sintering process for low-cost fly ash based ceramic microfiltration membrane in oil-in-water emulsion treatment[J]. *Sep Purif Technol*, 2019, 210: 511–520.
- [35] MESTRE S, GOZALBO A, LORENTE-AYZA M M, et al. Low-cost ceramic membranes: A research opportunity for industrial application [J]. *J Eur Ceram Soc*, 2019, 39(12): 3392–3407.
- [36] ISSAOUI M, LIMOUSY L. Low-cost ceramic membranes: Synthesis, classifications, and applications[J]. *CR Chim*, 2019, 22(2/3): 175–187.