Journal of Membrane Science 515 (2016) 144–153

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Fabrication, characterization and separation properties of three-channel stainless steel hollow fiber membrane

Ming Wang, Ming-Ling Huang, Yue Cao, Xiao-Hua Ma, Zhen-Liang Xu *

State Key Laboratory of Chemical Engineering, Membrane Science and Engineering R&D Lab, Chemical Engineering Research Center, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

ARTICLE INFO

Article history:
Received 28 January 2016
Received in revised form
13 April 2016
Accepted 22 May 2016
Available online 26 May 2016

Keywords:
Non-solvent induced phase separation
Three-channel
Stainless steel
Hollow fiber membrane

ABSTRACT

The industrial applications of stainless steel single-channel hollow fiber (SCHF) membranes were confined by their restricted mechanical strength due to the small radial dimension. A stainless steel three-channel hollow fiber membrane (TCHF) was developed through the non-solvent induced phase separation (NIPS) method and then sintered in inert atmosphere. The combination of low mass transfer resistance of the SCHF membrane with high mechanical strength and large specific surface area of the new configuration enabled the TCHF membrane to overcome the weakness of mechanical strength without compromising other properties. The resultant TCHF sintered at 1100 °C showed a N_2 permeation of 3.2×10^{-4} mol/(m^2 s Pa) which was one order of magnitude higher than that of SCHF membrane and the fractural loading of 18.2N which was four times higher than that of SCHF membrane. The corrosion resistance tests proved the chemical stability in hostile fluids and the recycle performance confirmed the durability after tough cleaning several times. The rejection of starch wastewater was nearly 85% after a long-term operation, which showed the superior filtration performance. Therefore, stainless steel TCHF membrane exhibited great potentials in versatile applications such as microfiltration, gas separation, and catalytic reaction.

1. Introduction

Dense Palladium (Pd) membranes have drawn extensive attention in hydrogen purification and steam reforming reactors credited to their extraordinary permeability and marvelous selectivity to hydrogen as well as wide chemical compatibility with hydrocarbon [1–4]. Porous stainless steel (PSS) or porous ceramics serve as promising supports for dense Pd/Pd-alloy composite layers to improve the hydrogen transmembrane flux and lower the cost [3,5–8]. In particular, PSS is the more appropriate support due to its high cracking resistance, almost the same thermal expansion coefficient as Pd, moderate operability at high temperature or pressure and flexibility for module construction and sealing [9]. The current major geometric structures of PSS are flat sheet, tube and SCHF membrane. Flat sheet membrane is subjected to its low specific surface area [10]. Although tube membrane fabricated by paste extrusion technique has high specific surface area and good mechanical strength, the thick tube wall which generates high mass transfer resistance and low packing density also compromises their large-scale applications. Theoretically, SCHF membrane fabricated by NIPS is the preferable substitute because of its high permeation flux and packing density. However, the insufficient of SCHF membrane in mechanical property disables SCHF membrane to meet the industrial demands. Researchers have developed a feasible route with the development of multi-channel hollow fiber (MCHF) membrane to overcome the drawbacks of conventional SCHF membrane [10–12]. For example, a TCHF membrane with consistent configuration and structures generates the equivalent of three SCHF membranes [13]. MCHF membrane is desirable where excellent mechanical strength, high permeation flux, energy saving, great durability, large packing density and convenient module construction are prerequisites. A comparative study between SCHF and MCHF membranes has been done by researchers [14].

Multi-channel organic HF membranes have been industrialized [15,16] and commercialized by some corporations such as BASF [17] and Hyflux [18] in last decades. The products are so stable and resilient that no single fiber breakage has occurred since they are industrialized in the first ultrafiltration plant [16]. Moreover, various configurations and dimensions of multi-channel organic HF membranes have been prepared by many groups, especially Chung's group [19–21] having made a contribution to the fabrication of HF membrane with different geometric structures. Nevertheless, when it comes to multi-channel inorganic HF membrane, there are finite literatures. Gu's group [12] prepared

* Corresponding author.
E-mail address: chemxuzl@ecust.edu.cn (Z.-L. Xu).

http://dx.doi.org/10.1016/j.memsci.2016.05.038
0376-7388/

four-channel Al_2O_3 HF membrane successfully and investigated the effects of air gap and sintering temperature on the properties of membrane. Li's group [11] prepared multi-channel capillary and monoliths with the similar micro-structures existing in SCHF membrane and proved that multi-channel geometry can settle the current SCHF membrane's insufficient in bending strength. Jin's group [10] prepared mixed conducting MCHF membrane with high breaking loading, great sustainability and high oxygen flux. Thus it is not difficult to judge that multi-channel inorganic HF membrane has gradually aroused researchers' interests in last several years. It can also be expected that multi-channel inorganic HF membrane will play a significant role in future practical applications. Whereas, the extensive work on extending various material multi-channel inorganic HF membranes still need to be carried out. The preparation techniques need to be optimized as well.

NIPS is a critical technique for the fabrication of SCHF membrane. It creates a thin wall with asymmetric structures for instance finger-like subject region and sponge-like skin layer. In addition, macro-voids and sponge-like subject region may also exist in the asymmetric structures depending on the compositions of casting solution and the varieties of the inorganic particles [12]. These asymmetric structures result in low mass transfer resistance. What's more, SCHF membrane also has higher packing density than tube and flat sheet membrane. Therefore, the combination of the micro-structures of SCHF membrane with the aforementioned features of MCHF membrane is in favor of MCHF's industrial applications.

In this study, stainless steel HF membrane with new configuration has been fabricated through NIPS technique and then sintered in inert atmosphere. The as-prepared stainless steel TCHF membrane exhibits superior fractural strength which makes up the weakness of SCHF membrane. The permeation flux is also enhanced with the increase of specific surface area. Herein, sintering temperatures, micro-structures, fractural strength, pore size distributions and permeation flux have been investigated systematically. Moreover, the corrosive resistance and practical application of pristine HF membrane are investigated as well.

2. Experimental

2.1. Materials

316L stainless steel powder (SSP, d_{50}=9.4 μm, Advanced Technology & Materials Co., Ltd.), N-methyl-2-pyrrolidone (NMP, Sinopharm Chemical Reagent Co., Ltd) and polyethersulfone (PES, BASF6020) were served as raw material, solvent and polymeric binder, respectively. Polyvinylpyrrolidone (PVP K90, BASF) was used to enhance the viscosity. SSP was put in 60 °C oven for 24 h before use. Self-made deionized water acted as the internal and external coagulation bath. All other reagents were used without pretreatment.

2.2. Preparation of stainless steel TCHF membrane

Generally, PES and PVP dissolved in NMP forming a homogeneous and moderate viscosity polymer solution under a mechanical rabbling. SSP was gradually added to the above solution to form a fine dispersed suspension. The mass ratio of the solution was SSP: NMP: PES: PVP=70:22.5:7:0.5 [22]. Before spinning, the suspension needed vacuum degassing for 30 min. Then the suspension was poured into a tubular vessel and pressed out through the special three-bore spinneret under nitrogen pressure of 0.1–0.2 MPa. Meanwhile, self-made deionized water was introduced into the bore of the spinneret via peristaltic pump for the gelation

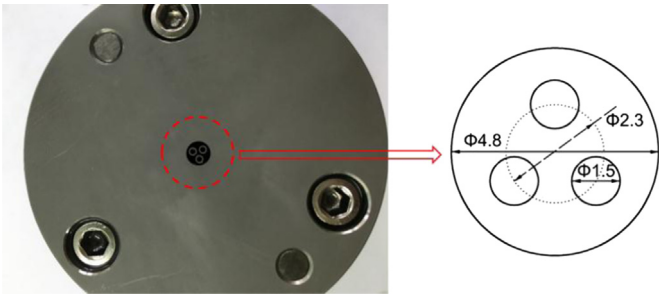

Fig. 1. The parameters of the three-bore spinneret. (Left: bottom real view; right: bottom schematic view).

of the inner surface and the air gap was 2 cm. The parameters of the new configuration spinneret are illustrated in Fig. 1 in detail. The green fibers were soaked in deionized water for 24 h to remove the residual solvent, and dried at 60 °C for 12 h, then calcined using an atmosphere furnace (Shanghai HAOYUE Co., Ltd.) to acquire the desired mechanical strength. The sintering temperature firstly reached to 600 °C at the heating rate of 1 °C/min and hold for 1 h to burnout the polymer completely, and raised to 1000 °C, 1050 °C, 1100 °C, 1150 °C, 1200 °C and 1300 °C respectively at the heating rate of 5 °C/min and hold for 1 h or 4 h at the nitrogen flow rate of 200 ml/min, then cooled naturally. In addition, SCHF membrane was prepared with a single-bore spinneret. Other operation processes were the same as that for three-channel HF membrane.

2.3. Characterization

Morphologies and micro-structures were reflected by the images of scanning electron microscopy (SEM, JEOL Model JSM-6380 LV, Japan). The samples were attached to a copper holder with conductive adhesives. The green compacts needed to be sputtered with platinum under vacuum condition.

Crystal phase was characterized through X-ray diffraction device (XRD, Mini-Flex 600, Japan). The device employed Cu Kα radiation under the voltage of 40 kV and the current of 100 mA within 2θ range of 20–80°.

Thermo gravimetric analysis was conducted via SDT Q600 to record the weight loss of green compact. The process operated under nitrogen atmosphere at the heating rate 5 °C/min ranging from 25 °C to 900 °C.

UV–vis absorbance was measured with UV-1800 (SHIMADZU, Japan). The relationship between the absorbance and concentration was correlated by the standard curve based on the Lambert Beer law. The standard curve needed to be measured in advance.

Pore size distributions were measured with capillary flow porosimetry (Beishide instrument 3H-2000PB, China) which conformed the standard of ASTM F316. The principle was based on the differential pressure and corresponding flow whereby the wetting liquid (ultra-pure water) was extruded out the pores of the HF membrane.

Mass transfer properties were characterized based on pure water flux (PWF) measured by a cross-flow module (Fig. 2) and nitrogen permeation measured by the porosimetry instrument.

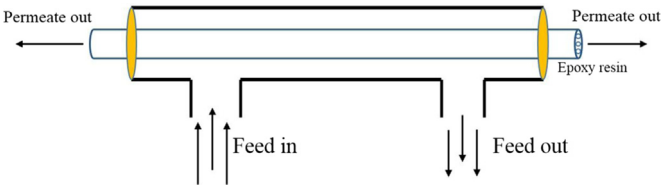

Fig. 2. Schematic diagram of the cross-flow module.