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Preparation and characterization of hydrophobic alumina planar membranes for water desalination

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Abstract

A planar alumina membrane was prepared by a one-step phase-inversion tape casting method. The membrane consisted of a thick support layer with finger-like large pores and a thin separation layer containing small pores with an average diameter of ~0.76 μm. The overall porosity of the membrane was ~59%, as determined with the Archimedes method, and the porosity associated with the large, finger-like pores in the support layer was ~34% as derived from image analysis. The surface of this alumina membrane was converted from hydrophilic to hydrophobic via grafting with a fluoroalkylsilane. The water desalination performance was tested by exposing the hydrophobic separation layer to an aqueous solution of 2 wt.% NaCl at 80 °C, while a sweep of distilled water at 20 °C was used, resulting in a water flux of 19.1 L m^{-2} h^{-1} and a salt rejection over 99.5%. Due to the excellent water desalination performance, the hydrophobic porous ceramic membrane holds promise for practical applications.

Keywords: Phase-inversion tape casting; Alumina; Surface grafting; Hydrophobicity; Membrane distillation

1. Introduction

In view of the global shortage of clean water, it is highly recommended to develop new methods for water treatment.[1,2] Compared with conventional separation processes like reverse osmosis or thermal evaporation, membrane distillation (MD) is expected to be a cost-effective technology for seawater desalination, due to low demands on heat source and operating pressure. Hydrophobic materials, such as polypropylene (PP), polytetrafluoroethylene (PTFE), polyvinylidenefluoride (PVDF), are widely used as MD material.[3] In comparison with polymers, hydrophobic ceramic membranes are much more desirable owing to their better chemical and thermal stability. Most ceramic membranes are naturally hydrophilic because of the surface hydroxyl. Therefore, they have to be modified with low surface energy materials before used for MD. The first work on hydrophobic ceramic membranes for membrane distillation was reported by Larbot in 2004.[4] Since then, a few ceramic membranes have been successfully prepared and applied in MD for water desalination, resulting in salt rejections of more than 95%.[5–7] However, MD also has some drawbacks such as low flux and high susceptibility to variation of salt concentration and feed temperature.[8] In general hydrophobic ceramic membranes with large flux, excellent salt rejection, sufficient mechanical strength and chemical stability are required for MD application.[9]

It is well known that mass transfer through a membrane largely depends on its thickness, porosity and pore size distribution.[10] It is desired to use a porous ceramic membrane with small transport resistance. Typically, a porous ceramic membrane consists of a multi-layered asymmetric structure: one or more thin top layers with small pores, enabling separation, and a thick bulk layer with large pores providing mechanical strength.[11,12] Very often the fabrication of such an asymmetric structure involves multiple steps. A support layer is first prepared, followed by coating an intermediate layer and application

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of the final separation layer. Each step involves high temperature sintering, making the ceramic membrane fabrication expensive. Clearly, combining the multiple steps into a single one is desirable in reducing production time and costs.

Recently, it is reported that ceramic membranes with the as-above described asymmetric structure can be prepared conveniently by phase-inversion tape casting.[13,14] Here a slurry of a ceramic powder in an organic polymer solution is cast on a temporary substrate, and then immersed into a water bath in which the organic polymer solution separates into a polymer-rich phase and a polymer-lean phase as a result of exchange of organic solvent with water. The slurry is solidified into a green tape due to the occurrence of the polymer-rich phase, and large finger-like pores are created in the green tape after removal of the polymer-lean phase. Since the phase-inversion process initiates from the slurry–water interface and proceeds into the bulk, the as-formed green tape possesses a two-layered structure: a thick layer containing finger-like large pores over a thin layer free of large pores. This asymmetric two-layered structure is preserved after firing of the green tape at elevated temperatures.

In the present study, porous alumina with asymmetric two-layered structure was formed using the phase-inversion tape casting method, and the surface of the alumina was further modified with a hydrophobic fluoroalkylsilane (FAS). The gas/liquid permeation as well as MD desalination properties of the as-prepared membrane was studied.

2. Experimental

2.1. Fabrication of alumina planar membranes

Phase inversion-tape casting method was used to fabricate the membranes. Details can be found elsewhere.[14] Briefly, polyethersulfone (6.2 wt.%) (PES) (Gafone 3000, Solvay Advanced Polymers) and polyvinylpyrrolidone (0.9 wt.%) (PVP) (K30, CP, Sinopharm Chemical Reagent Co.) were dissolved in N-methyl-2-pyrrolidone (31.0 wt.%) (NMP) (CP, Sinopharm Chemical Reagent Co., China) to form a stable polymer solution. Subsequently α-Al_2O_3 powder (61.9 wt.%) with an average particle size of 0.8 μm (Zhenghai, Jiangsu, China) was added to the solution. This mixture was mixed/milled for 48 h at room temperature, using a planetary mill. The as-prepared slurry was degassed for 10 min using a vacuum pump (2XZ-2, Tanshi, Linhai, China), and then casted on a Mylar sheet with a doctor blade of gap height 1.0 mm and motion speed 20 cm/min. The casted slurry was immediately immersed in water at room temperature and left for 24 h for coagulation. After drying under ambient conditions, the green tape was cut into round pieces with a diameter of 40 mm, then heated at a rate of 2 °C/min to 800 °C and kept at this temperature for 4 h to remove the polymer binder, followed by heating to 1500 °C at a rate of 2 °C/min and being held for 10 h. The samples were cooled down to room temperature at a rate of 2 °C/min. The whole sintering procedure was processed in air.

2.2. Surface grafting with fluoroalkylsilanes

Prior to surface grafting, the sintered alumina wafers were ultrasonically cleaned respectively in acetone, ethanol and water for 10 min. The wafers were dried at 100 °C for 2 h, immersed into a 2 wt.% FAS (1H,1H,2H,2H-perfluorooctyltriethoxysilane, DYNASYLAN, F8261) in ethanol solution at room temperature and left in this solution for 24 h to allow the coupling reaction to occur. After immersion the wafers were dried at 100 °C for 6 h. The immersion and drying processes were repeated three times. Finally, the membranes were stored at room temperature and ready for water desalination experiments.

2.3. Characterization

The dried green tape was analyzed using TGA and DSC (DTG-60H, Shimadzu). A sample was heated from room temperature to 1400 °C at a rate of 5 °C/min in air. Densification of the green body was analyzed by a dilatometer (DIL 402 C, Netzsch). A strip of green tape with a length of 9 mm a width of 3 mm and a thickness of 0.78 mm was heated to 1500 °C at a rate of 5 °C/min, the contraction along the length direction was measured with the increase of temperature.

The morphology of green tape and ceramic wafer was observed with scanning electron microscopy (SEM; JSM-6700F, JEOL, Japan) at an accelerating voltage of 20 kV. Prior to SEM observations the samples were covered with gold by means of sputtering.

The density of the ceramic wafer, ρ, was measured using the Archimedes method in mercury. The porosity was calculated using the formula $(1 - \rho/\rho_{th}) \times 100\%$ where ρ_{th} is the theoretical density of α-alumina. The porosity was also determined from images taken from back-scattered electron (BSE) mode of the SEM, using the Otsu's method as described elsewhere.[15] Otsu's method is a threshold selection method from gray-level histograms to distinguish different phases in an image. A better contrast between solid and pore can be obtained by using BSE image compared with secondary electron images. Finally the pore size distribution of the ceramic wafer was measured by the bubble point method.[16]

Nitrogen gas and pure water flux through ceramic wafers with a diameter of 20 mm were analyzed using a home-made equipment. A sample was fixed on a male connector, and then covered by a refined cylinder. Nitrogen was fed into the cylinder at various pressures, and the amount of permeated N_2 was measured with a soap bubble flow meter. Similarly, pure water permeation tests were performed and the weight of the permeated water was measured by an electronic balance.

The water contact angles of the membranes before and after grafting were measured using a contact angle meter (SL200B, Chenghui, China). The volume of a deionized water droplet was ~5 μL, and the average value of five measurements, performed at different positions on the same sample, was adopted as the contact angle.

Direct contact membrane distillation (DCMD) experiments were conducted using a home-made MD set-up, as shown in