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Microbubble formation using asymmetric Shirasu porous glass (SPG) membranes and porous ceramic membranes—A comparative study

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ABSTRACT

We have recently proposed a new method for generating uniformly sized microbubbles from Shirasu porous glass (SPG) membranes with a narrow pore size distribution. In this study, to obtain a high gas permeation rate through SPG membranes in microbubble formation process, asymmetric SPG membranes were used. At the transmembrane/bubble point pressure ratio of less than 1.50, uniformly sized microbubbles with a bubble/pore diameter ratio of approximately 9 were generated from an asymmetric SPG membrane with a mean pore diameter of 1.58 μm and a skin-layer thickness of 12 ± 2 μm at a gaseous-phase flux of 2.1–24.6 $\mathrm{m^3\,m^{-2}\,h^{-1}}$, which was much higher than that through a symmetric SPG membrane with the same pore diameter. This is mainly due to the much smaller membrane resistance of the asymmetric SPG membrane. Only 0.27–0.43% of the pores of the asymmetric SPG membrane was active under the same conditions. The proportion of active pores increased with a decrease in the thickness of skin layer. In contrast to the microbubble formation from asymmetric SPG membranes, polydispersed larger bubbles were generated from asymmetric porous ceramic membranes used in this study, due to the surface defects on the skin layer. The surface defects were observed by the scanning electron microscopy and detected by the bubble point method.

1. Introduction

Shirasu porous glass (SPG) membranes [1,2] are prepared by phase separation of Na_2O–CaO–MgO–Al_2O_3–B_2O_3–SiO_2 type glasses, which are made of Shirasu [1], calcium carbonate and boric acid. Shirasu is a volcanic ash that occurs naturally in the southern area of Kyushu in Japan, containing mainly SiO_2 and Al_2O_3. The Na_2O–CaO–MgO–Al_2O_3–B_2O_3–SiO_2 type glass separates into an acid-soluble Na_2O–CaO–MgO–B_2O_3 glass phase and an acid-insoluble Al_2O_3–SiO_2 glass phase at certain compositions within a temperature range of 923–1023 K. The micropores of SPG membranes are formed by acid leaching of the soluble phase. SPG membranes have interconnected, uniformly sized cylindrical pores, reflecting the phase-separated microstructure of the Na_2O–CaO–MgO–Al_2O_3–B_2O_3–SiO_2 type glass. The mean pore diameter of SPG membranes is determined by the heat treatment conditions (the temperature and the holding time) and/or the chemical composition of the Na_2O–CaO–MgO–Al_2O_3–B_2O_3–SiO_2 type glass [2].

SPG membranes find many applications as a separation membrane for microfiltration of oil-in-water emulsions and suspensions [3–5], a demulsification medium for water-in-oil emulsions [6], and especially as a dispersion medium in membrane emulsification [7,8] and gas dispersion process [9,10]. With the microbubble formation process, a gaseous phase is forced through an SPG membrane into a water phase and consequently size-controlled microbubbles are generated at the interface between the membrane surface and water phase under suitable conditions. The advantages of this technique are that the resultant bubble size and void fraction are mainly determined by the membrane pore size and membrane area, respectively [9]. This indicates that bubble size and void fraction can be optimized for a large-scale application.

Microbubbles exhibit excellent gas-dissolution abilities owing to a larger gas–water interfacial area and a longer stagnation compared to conventional larger bubbles. Hence, it is expected that the formation of microbubbles increases the efficiency of gas–liquid contact devices including bubble columns, chemical reactors, gas absorbents and fermentors. Additionally, in the medical and pharmaceutical fields, microbubbles are applicable to ultrasound contrast agents and targeted drug delivery carriers [11–14]. The control of bubble size and void fraction is significantly important in these applications. For this reason, SPG membranes are potentially suitable membranes for microbubble formation. However, microbubble formation process using SPG membranes suffers from low gas permeation rate, which is associated with both the symmetry structure of SPG membranes [2] and the necessity to prevent the continuous outflow of gaseous phase through the pores at higher transmembrane pressures [9]. Another cause of the low gas

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Nomenclature

A	effective membrane area (m^2)
C_∞	bulk solubility of gas through the water phase ($kg\,m^{-3}$)
D_b	mean bubble diameter (m)
^nD_b	bubble diameter at n% of the cumulative volume (m)
D_g	molecular diffusion coefficient of gas ($m^2\,s^{-1}$)
D_p	mean pore diameter (m)
J_g	gaseous-phase flux through the membrane ($m^3\,m^{-2}\,s^{-1}$)
J_w	pure water flux through the membrane ($m^3\,m^{-2}\,s^{-1}$)
k	proportion of active pores
k_m	maximum proportion of active pores
P_{BP}	bubble point pressure (Pa)
ΔP	transmembrane pressure (Pa)
Q	volumetric gas flow rate ($m^3\,s^{-1}$)
r_b	bubble radius (m)
R_m	membrane resistance (m^{-1})
V_g	molar volume of gas ($m^3\,mol^{-1}$)
V_p	pore volume of the membrane per unit mass of membrane ($m^3\,kg^{-1}$)
Δx	membrane thickness (m)
z	distance between the centers of adjacent active pores (m)

Greek letters

γ	surface tension ($N\,m^{-1}$)
δ	span of bubble size distribution
ε	membrane porosity
η_g	viscosity of gaseous phase (Pa s)
η_w	viscosity of pure water (Pa s)
θ	contact angle between the membrane surface and water phase (°)
ρ_G	true density of the membrane ($kg\,m^{-3}$)
τ	pore tortuosity
ω	Ostwald-ripening rate

Subscripts

b	bubble
g	gaseous phase
p	membrane pore
int	intermediate layer of he asymmetric membrane
skin	skin layer of the asymmetric membrane
sup	support layer of the asymmetric membrane

permeation rate is the small proportion of active pores, which is defined as the proportion of bubble-forming pores to all pores [10,15]. As an example, the proportion of active pores was only 0.27–0.44% at a gaseous-phase (air) flux of 0.21–6.08 $m^3\,m^{-2}\,h^{-1}$ through an SPG membrane with a mean pore diameter of 5.0 μm into a 2.0 mol m^{-3} Tween 20 (polyoxyethylene (20) sorbitan monolaurate) solution within a transmembrane/bubble point pressure ratio range of 1.03–1.53 [16]. For economic reasons, the gas permeation rate through a given membrane area at a given transmembrane pressure should be as high as possible to minimize investment costs. To increase the gas permeation rate, SPG membrane structure must be asymmetric, which leads to reduce the membrane resistance. Recently, we have developed a new type of asymmetric SPG membranes, which have a thin porous glass layer with a smaller pore size, supported by a thick porous glass layer with a larger pore size [17]. Our previous study on membrane emulsification showed that a high dispersed-phase flux through an asymmetric SPG membrane was obtained, due to the much smaller membrane resistance of asymmetric SPG membrane than that of symmetric (conventional) SPG membrane [17]. However, there has been no study on the use of asymmetric SPG membranes to increase a gaseous-phase flux in microbubble formation.

The primary objective of the present study is therefore to obtain a high gas permeation rate in microbubble formation by using asymmetric SPG membranes. The secondary objective is to compare microbubble formation from asymmetric SPG membranes with that from asymmetric porous ceramic membranes. Typically, porous ceramic membranes have a multi-layered asymmetric structure to obtain a high permeability of gas or liquid. For example, a two-layered ceramic membrane comprises a very thin skin layer and a porous thick layer. Most commercial ceramic membranes are made up by a slip coating-sintering method and have pore diameters of 10 nm to 10 μm. Other techniques including sol–gel method are used to prepare asymmetric ceramic membranes with pore diameters of 1–10 nm. With the slip coating-sintering method, a porous ceramic substrate is made by pouring a dispersion composed of fine ceramic grains and an organic binder into a mold, and then by sintering at high temperatures. One surface of the resultant substrate is coated with a suspension comprising finer particles and a binder solution. After drying and sintering at high temperatures, microporous skin layer is formed on the porous ceramic tube. The pore morphology of ceramic membranes substantially differs from that of asymmetric SPG membranes because the pores of ceramic membranes are the voids between the ceramic particles. In the present study, we attempted to generate microbubbles using asymmetric SPG membranes and asymmetric porous ceramic membranes. The influence of membrane structure on the microbubble formation process was investigated and compared.

2. Experimental

2.1. Membranes

In our laboratory, four asymmetric tubular SPG membranes with different pore sizes and different thicknesses of the skin layer were prepared from two primary glasses in the $NaO–CaO–Al_2O_3–B_2O_3–ZrO_2–SiO_2$ system with different growth rates of phase separation as listed in Table 1. All these SPG membranes had a length of 35 mm and an inner diameter of 4.6 mm. The preparation procedures were performed as previously described [17]. The primary glass separates into an acid-soluble $NaO–CaO–B_2O_3$ glass phase and an acid-insoluble $Al_2O_3–ZrO_2–SiO_2$ glass phase at certain chemical compositions within a temperature range of 923–1023 K. With an increase in the Al_2O_3 content the phase separation growth rate of the primary glass decreases and thus the resultant (symmetric) SPG membranes have smaller pore sizes, while with an increase in the B_2O_3 content the phase separation growth rate increases and thus the resultant membranes have larger pore sizes [1,18,19]. Therefore, the Al_2O_3-rich and B_2O_3-rich primary glasses were laminated in two layers to be formed into a tube at 1373 K by the blowing method. The pore size of the skin layer of asymmetric SPG membranes can be controlled by adjusting the heat treatment conditions [17]. The pore size increases with increasing heat-treatment temperature and/or the holding time. Therefore, the resultant glass tube was heat-treated at 993 K for 30 h to cause the phase separation, and subsequently leached out with a 0.5 mol dm^{-3} hydrochloric acid at 303 K, after which asymmetric tubular SPG membrane, AC-1 with a skin-layer pore diameter of 0.63 μm was obtained. Similarly, the AG-2, AG-3 and AG-4 membranes with a skin-layer pore diameter of 1.58 μm were prepared by heat-treatment of the primary glasses at 1018 K for 30 h and subsequent acid leaching. The thickness of the skin layer was controlled by varying the volume