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High-selectivity, high-flexibility glass hollow-fiber membrane for gas separation

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A high gas selectivity, high flexibility glass hollow-fiber membrane based on spinodal phase separation has been prepared by direct winding from glass melt, followed by acid leaching processing.

Because of their stability in organic solvents and at high temperatures, inorganic membranes have attracted much attention as a subject of research. Many inorganic membranes with high gas selectivity[1] have been prepared by a variety of methods such as sol–gel processing,[2] chemical vapor deposition,[3] physical vapor deposition[4] and hydrothermal synthesis.[5] However, only a few inorganic membranes have reached market acceptance because of the complicated processing and high manufacturing costs involved.

About ten years ago, glass hollow-fiber membranes, which had high selectivity for gases, were reported.[6,7] The gas separation properties and physical properties of these membranes were investigated.[7] However, the composition of the glass hollow-fibers and the process for making glass hollow-fibers were not clearly indicated. Recently, the preparation of glasses with "ultra micropores" (pore diameter less than 1 nm) and the effect of cooling rate on pore distribution in quenched sodium borosilicate glasses were reported.[8,9] The investigated glass compositions were those in which spinodal phase separation is well known to occur. It was concluded that the origin of ultra-micropores of these glasses were created by spinodal phase separation during the cooling, and that pore size based on spinodal phase separation decreased as the cooling rate increased. To apply these results and to achieve practical use in a actual system, we have developed a glass hollow-fiber membrane prepared by direct winding from glass melt, followed by an acid leaching process. Shaping into a hollow fiber has the following advantages: it provides a large membrane area and a compact module (high membrane area per membrane module volume due to their small diameter); it endows flexibility; and it allows a high shaping rate (several hundred meters per minute). These properties should facilitate the mass production of glass hollow-fiber membranes.

In the present report, we describe the preparation of an ultra microporous glass hollow-fiber membrane, and its novel, high gas separation properties.

The membrane was formed from a glass hollow-fiber with an outer diameter of about 70 μm and an inner diameter of about 50 μm. The composition of the glass hollow-fiber was 57.5% SiO_2–5.0% ZrO_2–28.3% B_2O_3–9.2% Na_2O by weight. The hollow fiber was prepared from a glass melt using the apparatus shown in Fig. 1. A Pt double crucible containing glass cullet was preheated in an electric furnace to melt the glass and then maintained at 1473 K. Dried air was supplied inside a Pt double crucible to make the glass fiber hollow. When the melted glass was poured from the nozzle of the crucible, it was wound up by the stainless steel drum. The drawing speed was about 50 m min^{-1}. The glass hollow-fiber was cut into lengths of about 400 mm and immersed in a solution of 3 mol dm^{-3} HNO_3 at 371 K for 10 min until the sodium and boron ions were completely eluted. The acid/glass ratio, defined as the ratio of the volume of leaching acid to the weight of glass hollow-fibers, was kept constant at 2000 cm^3 g^{-1}. After acid leaching, the fibers were washed with distilled water and dried at room temperature. A SEM photograph of the glass hollow-fiber membrane prepared by acid leaching is shown in Fig. 2. The cross section of the membrane was circular, and the membrane surface was smooth with no macrocracks observed after the leaching treatment. It was found that the membrane had ultra micropores (pore diameter less than 1 nm) from nitrogen adsorption measurement. The prepared membranes were flexible as shown in Fig. 3. A 2 cm ring could be formed by tying fiber ends together. This flexibility is a novel property of the glass hollow-fiber membrane and important for making a module.

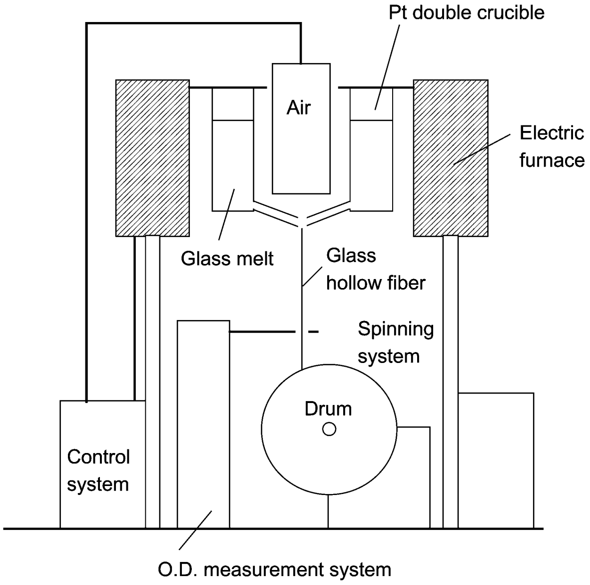

Fig. 1 Schematic diagram of the apparatus for making glass hollow-fibers.

Single gas permeation through the membrane was measured at 373, 423 and 473 K using He, N_2, CO_2, O_2 and CH_4 by a variable-pressure method.[10] One side of the glass hollow-fiber membrane was sealed and the other side connected to a Pyrex glass tube with epoxy resin. This membrane module was supported in a gas flow cell. Before the permeation measure-

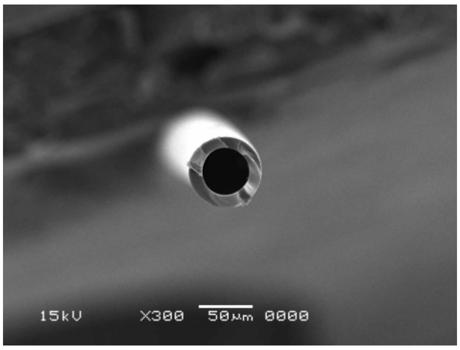

Fig. 2 SEM photograph of the glass hollow-fiber membrane.

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Table 1 Permeance and selectivity through the glass hollow-fiber membrane

	10^{11} × Permeance/mol m^{-2} s^{-1} Pa^{-1}						Selectivity				
Temperature/K	N_2	He	H_2	CO_2	O_2	CH_4	He/N_2	H_2N_2	CO_2/N_2	O_2/N_2	CO_2/CH_4
373	0.060	110	67	4.0	0.74	N.D.	1800	1100	67	12	—
423	0.12	150	90	4.4	1.1	N.D.	1300	750	37	9.2	—
473	0.19	180	110	4.4	1.3	0.016	950	580	23	6.8	280

N.D.: Not Detected.

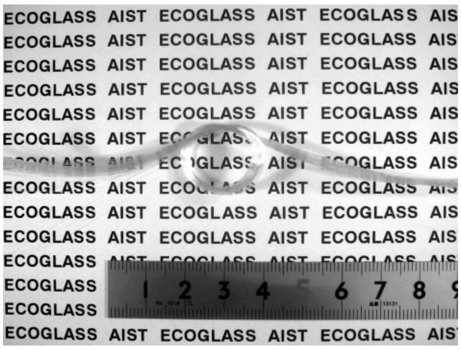

Fig. 3 Photograph of the glass hollow-fiber membrane.

ment, the membrane was dried at 473 K in a vacuum to remove adsorbed moisture from the micropores. Table 1 shows the single gas permeances of He, N_2, CO_2, O_2 and CH_4 through the glass hollow-fiber membrane at 373, 423 and 473 K. The table indicates the selectivity $\alpha = P_A/P_B$, where P_A and P_B are the permeance of gases A and B, respectively. The glass hollow-fiber membrane displayed high H_2, O_2 and CO_2 selectivity even at high temperature. The H_2/N_2 selectivity was 1100 at 373 K, 770 at 423 K and 590 at 473 K. This value at 373 K is around 300 times as large as the theoretical Knudsen value (H_2/N_2 = 3.7) and more than 2 times for the reported glass hollow-fiber membranes with high gas selectivity.[7] This high selectivity is due to optimized process control and the composition of glass for utilizing the spinodal phase separation. Utilization of the spinodal phase separation has the effect of suppressing defects and endows the membrane with a high strength thought to be sufficient for practical application. The relationship between the extent of spinodal phase separation and cooling rate, where the former decreases as the latter increases,[8] produces membrane pores small enough that only small molecules pass through.

The CO_2/CH_4 and O_2/N_2 selectivity were also higher than the theoretical Knudsen values ($CO_2/CH_4 = 0.60$, $O_2/N_2 = 0.94$). These values were high even at 473 K ($CO_2/CH_4 = 270$, $O_2/N_2 = 6.8$). The permeance of H_2 was 1.1×10^{-9} mol m^{-2} $s^{-1} \cdot Pa^{-1}$ at 473 K. From this value, a membrane module with an outer diameter of 10 cm and a length of 50 cm could pass about 5 m^3 h^{-1} (STP) (packing density 25%, pressure difference 1 MPa).

With the fabrication of membrane modules with glass sealing for high temperature usage having now started to develop, further such experiments will be needed, as this is the most important technology for the industrial application of the glass hollow-fiber membranes.

Success in forming of a hollow-fiber configuration and simplified processing with acid leaching serve to lend this inorganic membrane to production-scale manufacture. At an estimated cost of several tens of m^{-2}, these advantages make this membrane less expensive and would entail costs equivalent with that of organic membranes and less than one-tenth that of other inorganic membranes. The present results are promising for actual applications of glass hollow-fiber membranes in natural gas purification, biogas purification, CO_2 removal and H_2 purification.

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