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Development of ceramic support substrates for hydrogen separation membrane applications

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Production and separation of hydrogen are two of the processes with considerable opportunities for inorganic membrane applications. Methane reforming accounts for bulk of the hydrogen produced in the world today. It is well known that selective separation of hydrogen from the reforming reactor environment using supported membranes could make the reforming process more efficient. The development of porous supports over which membranes are made is a key step in the membrane development process. In this paper we have outlined the development history of tubular supports for hydrogen separation application under steam reforming condition. The properties of the substrate such as strength, thermal expansion and surface roughness are reported. To ascertain the performance of the system for steam reforming application, hydrothermal stability of the support system including the sealing material was measured in our laboratory. Details of the measurements and results are presented in this paper.

Key words: Membrane-reactor, Hydrogen production, Porous substrates, Hydrothermal stability, Methane reforming

1. INTRODUCTION

The production of hydrogen using membrane based reforming technology is set to become more and more important, as further applications based on the use of hydrogen emerge. Majority of hydrogen produced presently uses steam-reforming technology, run at rather high temperatures to get maximum efficiency out of the equilibrium-limited reaction. It is well known that the application of a membrane-based reformer would enable the reaction to run efficiently at temperatures as low as 773 K [1-3]. In order to achieve high efficiency the membrane must be capable of separating the product H_2 gas with high separation power (permeance and separation) and silica based membranes are considered as candidates for this [4-13]. Key properties in the selection of silica as the membrane material are its hydrogen separation ability and large hydrogen permeance at ~773 K. Moreover, microporous silica membranes could be made on a variety of substrate material surfaces.

Consequently, the performance of the silica membrane is closely linked to the quality and performance of the ceramic support substrate. The gas permeance of the membrane system is related to the resistance of the membrane as well as to that of the support system including any intermediate layer. For making high permeable membranes it is therefore important to fabricate a porous support system allowing high permeance. Moreover, the quality of the porous support will also govern the quality of the intermediate layer and hence its thickness.

The quality of the support and intermediate layer will also directly affect the separation performance of the membrane system. To realize large molecular selectivity values it is therefore important to make good quality supports with no surface irregularities and pinholes. The stability of the membrane system is very important for successful applications in high temperature environments like in membrane reactors. The stability of the membrane system is closely linked to the stability of the support. When feed gas is supplied through the support side, the stability of the support structure in the feed side environment of the separator/reactor is crucial. Even if the support is located in the permeate side of the membrane tube, hydrogen/hydrothermal stress experienced on the support will be high and good resistance against degradation is necessary.

The properties of the substrate such as porosity, pore-size and strength as well as hydrogen/hydrothermal stability are therefore important parameters in the development of membranes for high temperature applications. In this paper we have detailed the development of a porous alumina support substrate and its properties. The alumina supports were used for fabricating a tubular bundle by fixing the supports on dense alumina endplates using glass-based sealant materials. The characteristics of the tubular bundle as well as the gas permeation properties are detailed in the paper.

2. MATERIALS AND METHODS

A tubular porous substrate made of alpha alumina was initially developed. Alpha alumina powder of particle size 3.5 μm was used for making the support substrate. The particle size distribution of the powder is shown in Figure 1. The powder was mixed with methylcellulose binder and water to make the paste for extrusion. The extruded samples were dried and then sintered at 1673 K. Porous tubes of 6 mm outside diameter, 4mm inside diameter and 400 mm length were fabricated by this method. These supports were polished to obtain necessary surface quality for coating them with an "intermediate" support layer.

The intermediate layer was made from alpha alumina particles of average size 300 nm. These alumina particles were made into water-based slurry. Alumina tubular substrates were dip-coated with this slurry and sintered to make intermediate layers.

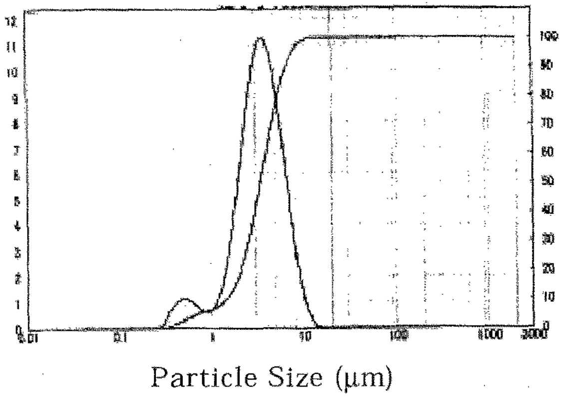


Fig.1: Size distribution of the alumina particles used for the substrate.

Tubular bundles were prepared by fixing alumina tubes (with intermediate layer) on dense alumina endplates using glass based sealant materials. The sealing temperature was higher than 1073 K. The thermal expansion coefficient of the selected glass sealant was comparable (< 20% change) to that of alumina.

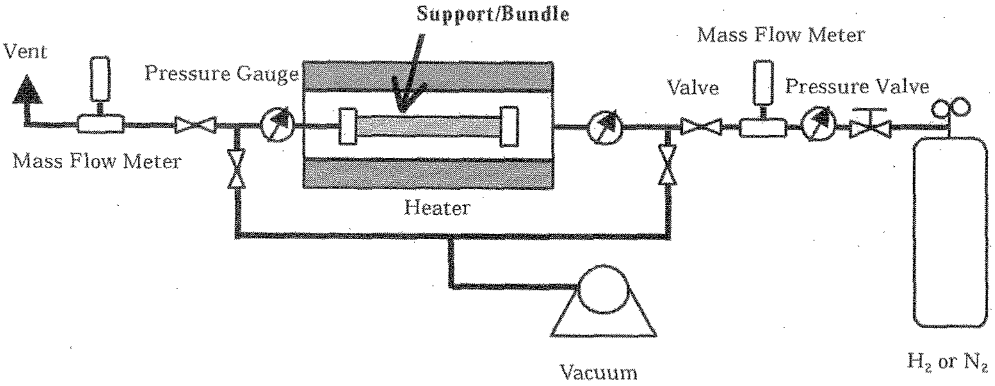


Fig.2: Set-up used for high-temperature gas permeation study

Gas permeation tests of the supports/bundles were carried out in a tubular module (Figure 2). H_2 or N_2 gas was flowed through the module at a pressure higher than 0.1 MPa and gas permeation rate was measured using flow meter. Permeation values in the temperature range RT-873 K were collected. Hydrothermal stability measurements were performed in a similar set-up. For the measurement, the membrane was initially heated to 773 K and held at that point. Hydrogen was then introduced into the chamber and kept for 5~24 hours at a pressure of 0.5 MPa. The feed gas was then replaced with equimolar mixture of H_2 and H_20. Module pressure was maintained at 0.5 MPa and the flow rate of H_2O and H_2 was maintained at around 0.15 mol/hour all through the measurement. Sample was kept under this atmosphere for >5hours. Dry H_2 gas permeation data was collected at the start/end of each step as well as bubble point data was collected before and after the measurement to ascertain the changes in properties.

3. RESULTS AND DISCUSSIONS

Tubular supports with the following properties were prepared. The porosity of the support was 40% and the pore size was 700 nm. The thermal expansion coefficient of the porous support was 7.6E-6 /K and the strength was around 30 MPa. The average surface roughness of the polished sample surface was around 340 nm. High-temperature gas permeation data are shown in Figure 3.

The porosity, pore-size and thermal expansion

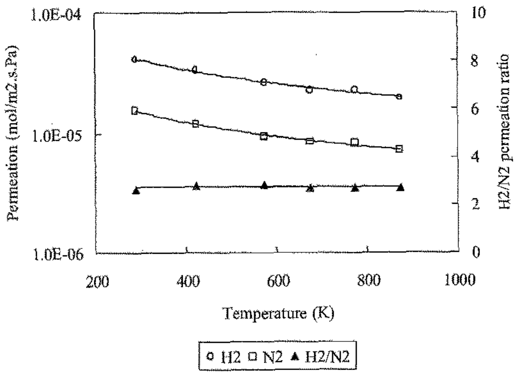


Fig.3: H_2 and N_2 gas permeation data of porous alumina supports.

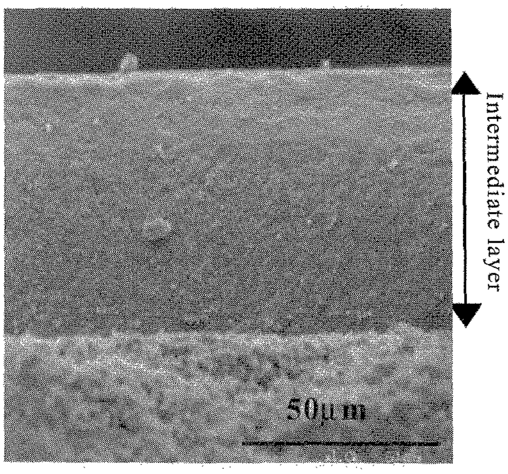


Figure 4: SEM picture of porous support coated with intermediate layer

coefficient of the intermediate layer was determined using appropriate samples made using the same batch of alumina powder and/or slurry. The pore size of the intermediate layer was measured as 60 nm and porosity as 39%. The thermal expansion coefficient was measured as 7.5E-6 /K. The average roughness of the intermediate layer coated support was around 160 nm. Figure 4 shows the cross-section of a coated support. From the figure it is clear that defect-free intermediate layers could be processed. Figure 5 shows the gas permeation data of the intermediate layer coated supports. It is shown that H_2 gas permeation values higher than 1E-5 mol/m^2.s.Pa could be measured.

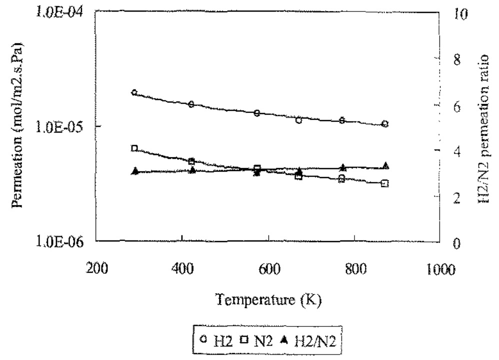
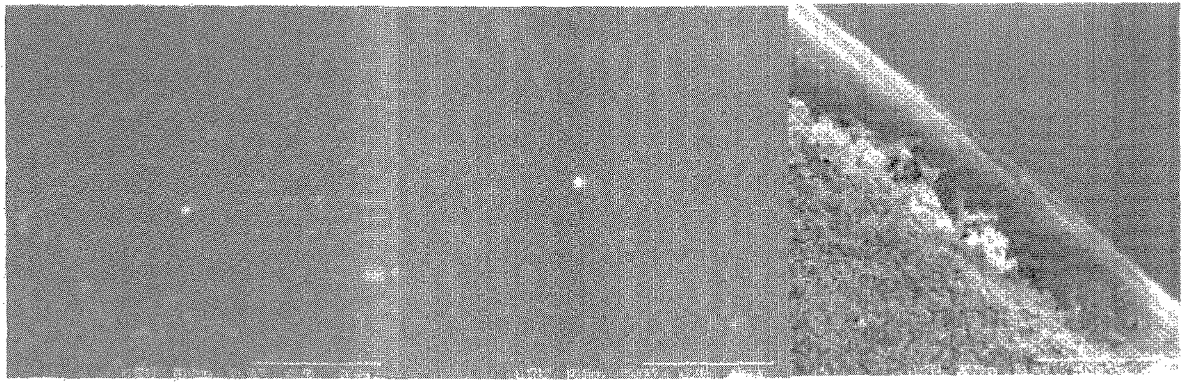


Figure 5: Gas permeation data of intermediate layer coated alumina supports.



Before After After

Figure 6: SEM of surface and cross-section of support coated with sealing material before and after hydrogen/hydrothermal stability measurement.

Hydrothermal stability measurements of the support substrates and the supports coated with intermediate layers were measured as described in the experimental section. No differences in gas permeation or bubble point pressure of the samples were observed after exposure to hydrogen and hydrothermal environment at 773 K.

Alumina substrate tubes coated with intermediate layers were used for fabricating tubular bundles. High temperature (glass based) sealant materials were used to connect the porous tubes and the endplates. The performance of the sealing materials and its hydrogen and hydrothermal stability were checked by separate experiments using a support coated fully with sealing material. The SEM pictures of the surface and cross-section of the sealing layer is shown in Figure 6. No visible alternations in the layer-structure or morphology occurred due to exposure to high temperature hydrogen and steam. No leakage was detected after the test confirming the good sealing performance.

The photograph of the alumina tubular bundle together with the schematic showing the configuration of the tubes is shown in Figure 7. The all-ceramic bundle has a peripheral volume of about 400 cc and weighed roughly 250 gm. Membrane area/ peripheral volume ratio of the bundle was 120 m^2/m^3.

The bundle was used for gas permeation studies as well as hydrothermal stability studies. These studies were carried out just as in the case of single support tubes. Hydrogen/hydrothermal stability studies evidenced the good stability of the bundles, as no changes in properties

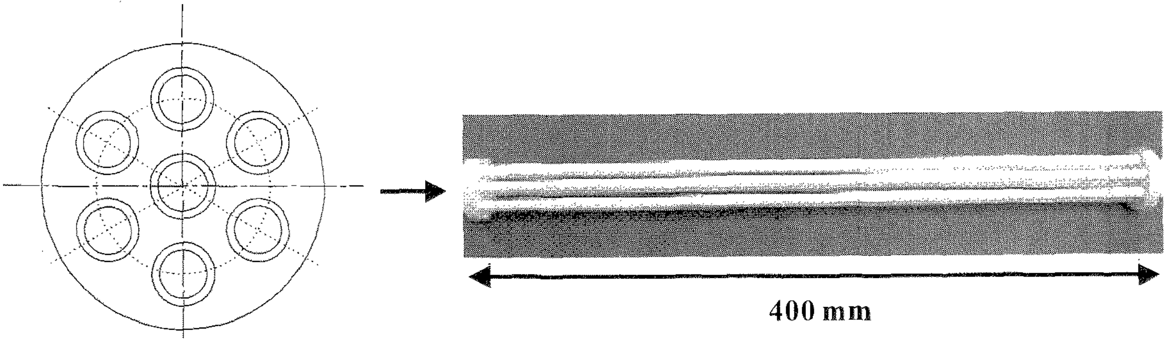


Fig. 7: Photograph of a tubular bundle and schematic of the configuration of tubes in the bundle.

were observed after the stability measurements. The gas permeation values were slightly lower than that of single tubes. Yet, hydrogen gas permeance values higher than 1E-5 mol/m^2.s.Pa were measured for the bundles consisting of intermediate layer-coated alumina supports.

These alumina tubular bundles were further coated with layers of gamma alumina and silica [14,15]. Microporous silica membrane bundles with no visible defects were produced by this method. The gas permeation data of a silica membrane bundle is shown in figure 8. Very high hydrogen permeance values were measured. However, the measured H_2/N_2 permeation ratio of ~12 is low compared to the values measured with tubular silica membranes [15]. Improvements in the processing of membranes over tubular bundles should be necessary.

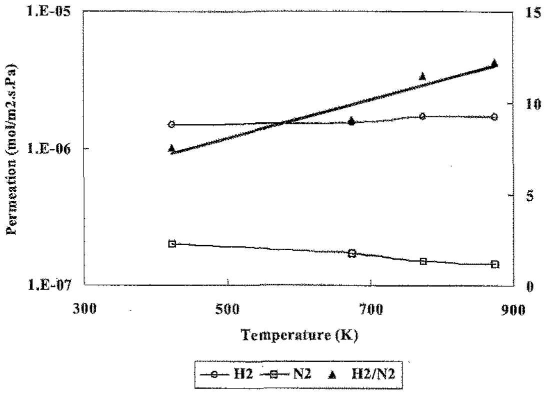


Fig. 8: Gas permeation data of a silica membrane bundle. As shown in the figure, hydrogen permeation value ~2E-6 mol/m^2.s.Pa was measured. This corresponds to a hydrogen flow value of 660 l/hour through the bundle at 0.1 MPa pressure, which should be enough to run a 1 kW class PEFC.

These silica membrane bundles could be used in a membrane based methane reformer. The in-situ separation of hydrogen from the reforming reactor environment using membranes as shown in Figure 9 should make the equilibrium-limited conversion process more efficient. Moreover, the application of membranes with high selectivity for hydrogen molecules compared to CO molecules should allow the use of permeate hydrogen gas directly in fuel cells without further CO stripping or selective oxidation. As shown in figure 8, in this study a hydrogen permeation value ~2E-6 mol/m^2.s.Pa was measured with silica membrane bundles. This corresponds to a hydrogen flow value of 660 l/hour through the bundle at 0.1 MPa pressure. This permeate flow should be enough to run a 1 kW class PEFC directly with hydrogen gas from a membrane reactor equipped with such a membrane bundle.

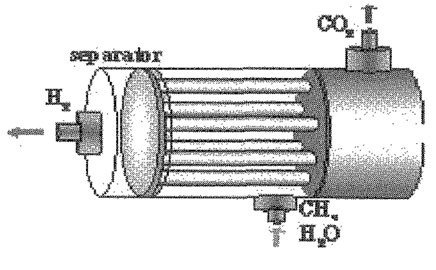


Figure 9: Schematic showing the configuration of a steam-reforming reactor equipped with a tubular membrane bundle. Ceramic membrane bundle similar to the one developed in this study could be used.

4.CONCLUSIONS

Porous alumina supports coated with intermediate layers were prepared and properties including gas permeation behavior were studied. Very high hydrogen permeation values together with good stability in hydrogen/hydrothermal atmosphere were measured. These alumina support tubes were used for fabricating tubular bundles. Glass based high temperature sealing material was used to connect the tubes to the end plates. Silica membrane modules made from these tubular bundles showed very high H_2 permeance. It is expected that such silica membrane modules will be usable in membrane reactors for the high temperature extraction of hydrogen from the reforming environment.

5.ACKNOWLEDGEMENTS

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