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Thin and defect-free Pd-based composite membrane without any interlayer and substrate penetration by a combined organic and inorganic process†

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Received (in Cambridge, UK) 26th September 2005, Accepted 17th January 2006
First published as an Advance Article on the web 27th January 2006
DOI: 10.1039/b513613j

A novel combined organic and inorganic process for preparing thin supported membrane was developed, using which a thin and defect-free Pd membrane with uniform thickness of 5 μm was directly coated onto porous α-Al_2O_3 hollow fiber without any interlayer and substrate penetration; at the same time, there existed a small interstice between membrane and substrate, which led to higher hydrogen permeance, infinite selectivity, and better membrane stability.

Thin membrane on a porous substrate is a hot research focus in the chemical separation field. Especially, the increasing demand for pure hydrogen in operating fuel cells, the great attraction of dehydrogenation and hydrogenation membrane reactions, prospective uses in producing hydrogen related fine chemicals, and the traditional application in petrochemical and metallurgical processes make the Pd-based membrane extremely important.[1–6] Prior to its industrialization, the Pd-based membrane must satisfy multiple objectives, such as delivering high hydrogen permeance, overcoming hydrogen embrittlement, showing mechanical/thermal/chemical stability, and lowering cost.[4]

A thin Pd-based composite membrane with a thin metal layer on a porous substrate is the best way to solve these problems.[7–13] However, due to the big surface pores of the substrate it is difficult to avoid pinholes during the preparation process, which leads to a much thicker Pd layer. Introducing a microporous interlayer is an effective method of solving this problem, but it greatly increases the gas permeation resistance. In addition, most of the present Pd-based composite membranes cannot be steadily operated at temperatures higher than 823 K due to intermetallic diffusion (porous metal substrates) and the peeling effect of the anchored metal layer (porous ceramic substrates).[5] Recently, Pd-based foil from cold-rolling technology was mechanically coated onto a porous substrate with a small interstice between the membrane and the substrate, showing higher permeability and better membrane stability.[14] But a thickness larger than 50 μm makes the hydrogen permeance too small and the membrane cost too high.

We have developed a combined organic and inorganic method of coating a thin and defect-free Pd membrane onto a big porous substrate without any interlayer and substrate penetration. A polymer precursor layer with an ultra smooth and tight surface was coated onto a porous substrate (α-Al_2O_3 hollow fiber supplied by NOK, od 2.9 mm, id 2.2 mm, pore size 150 nm, porosity 52%, and length 5–6 cm) using an activation solution consisting of Pd acetate (1.1 wt%), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, 5.3 wt%), and chloroform. It is obvious that the activation process is very different from the general process.[15] Pre-electroless plating was carried out using a commercial Pd-plating bath (PALLA TOP, Okuno Chemical Industries Co., Ltd.) at 323–343 K with a pH value of 5–6. The palladium salt is palladium chloride, the stabilizer is EDTA sodium, and the palladium concentration is 1–2 g/L. After that, the organic layer was removed by high temperature (873–1273 K) treatment in stagnant air, which resulted in a smaller interstice between the substrate and the pre-plated Pd layer. After formal electroless plating under the same conditions, the thin and defect-free Pd-based membrane was prepared. The surface morphology of the membrane was measured by SEM. The gas permeation behavior was tested using a single gas method at a temperature of 623–873 K with a pressure difference of 5–220 kPa. The membrane stability was evaluated.

Fig. 1(a) shows that the Pd membrane is ultra smooth and there are no obvious Pd crystal barriers and defects on the membrane surface. Fig. 1(b) shows that a uniform membrane thickness of about 5 μm was attained, and the membrane is completely dense. Moreover, there is an obvious and small interstice between the Pd membrane layer and the porous substrate, which is different from most other deposited membranes on porous substrates.[4] This small interstice may make the whole Pd membrane shift while enduring thermal cycles because force is put on the whole Pd layer rather than on the small Pd anchor in the pores, which can effectively enhance the membrane stability. Because there is no substrate penetration, the Pd effective inner area increases greatly, which is one of the key factors for high hydrogen permeance.

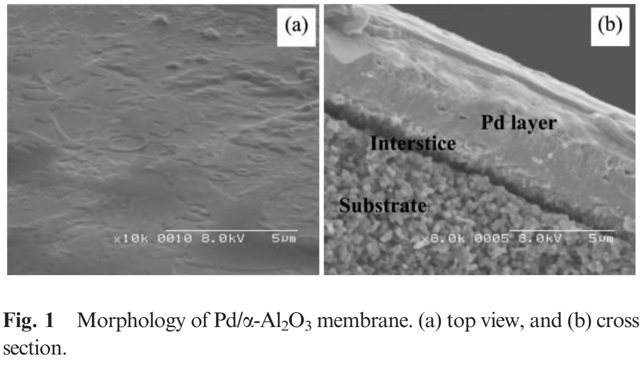

Fig. 1 Morphology of Pd/α-Al_2O_3 membrane. (a) top view, and (b) cross section.

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† Electronic supplementary information (ESI) available: Theoretical analysis of the membrane stability. See DOI: 10.1039/b513613j

The hydrogen flux *versus* the pressure difference at different temperatures is shown in Fig. 2. At 873 K with a pressure difference of 200 kPa, a flux as high as 0.82 mol m^{-2} s^{-1} was achieved. Compared with some other composite membranes under similar conditions, our Pd-based membrane has a relatively high hydrogen flux (Table 1). In addition, the *n* values in the permeation equation: $J = (Q/l)(P_H{}^n - P_L{}^n)$ for different temperatures were regressed. They approach 0.5 in the high temperature zone, but increase gradually with decreasing temperature. The activation energies for hydrogen permeation in the temperature ranges of 823–873 K and 623–673 K are 14.8 kJ/mol (n = 0.65) and 28.5 kJ/mol (n = 0.85), respectively.

The hydrogen flux of our Pd-based membrane *versus* operating time at 773 K with a pressure difference of 100 kPa is shown in Fig. 3(a), revealing that the hydrogen flux is relatively stable over a long operation time of 170 h. Moreover, the membrane stability was also measured using a gas exchanging cycle between hydrogen and helium and the results are shown in Fig. 3(b), showing that as many as 40 gas exchanging cycles did not impair the hydrogen permeation flux.

After all the permeation experiments, any helium leak is still undetectable at 773 K with a pressure difference of 300 kPa, revealing that the membrane is still defect-free and the hydrogen selectivity is still infinite.

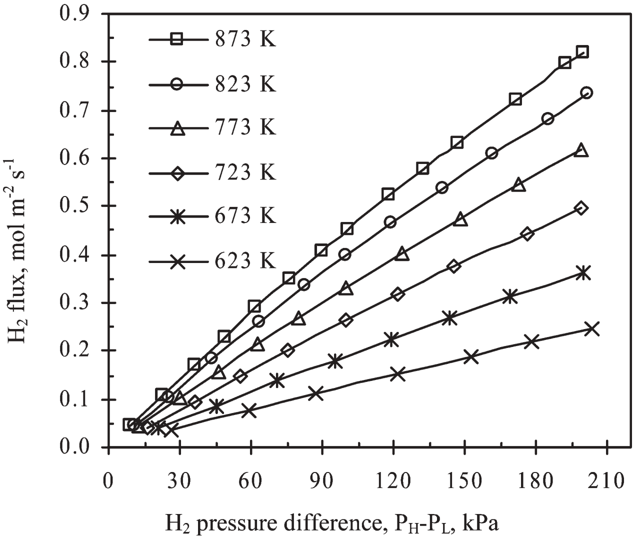

Fig. 2 Hydrogen flux *versus* hydrogen pressure difference at temperatures of 623–873 K for our Pd composite membrane.

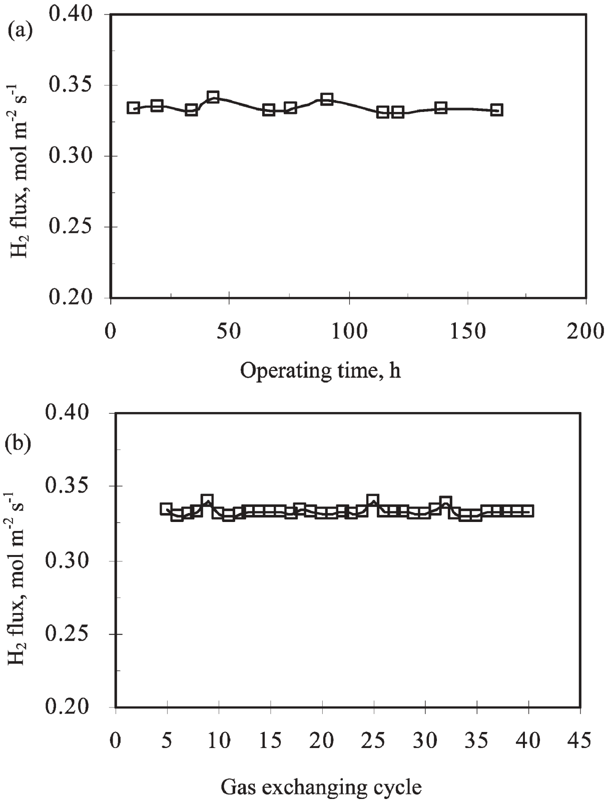

Fig. 3 Membrane stability designated by H_2 flux *versus* (a) operating time, and (b) gas exchanging cycles.

The excellent performance of our Pd-based membrane can be ascribed to the special membrane configuration, which resulted from the special combined organic and inorganic method. The preparation principle is shown in Fig. 4. Firstly, the fresh porous

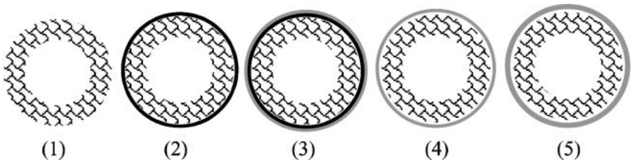

Fig. 4 Schematic of combined organic and inorganic process for preparing defect-free and uniform thin Pd membrane coated on porous substrate. Cross sections (1) substrate, (2) polymer layer + substrate, (3) Pd layer + polymer layer + substrate, (4) Pd layer + small interstice + substrate, and (5) defect-free Pd layer + small interstice + substrate.

Table 1 Comparison of the permeation results of different palladium-based composite membranes[a]

Membrane	Preparation method	Thickness, μm	Temperature, K	Driving force, kPa	H_2 flux, mol m^{-2} s^{-1}	Selectivity
Pd/PSS[6]	MD-ELP	6	773	100	0.260	∞ (H_2/N_2)
Pd/PSS[13]	ELP	10	753	100	0.089	1000 (H_2/N_2)
Pd/Al_2O_3[2]	ELP	7–15	673	100	0.086–0.134	100–1000 (H_2/N_2)
Pd–Ag foil[14]	Cold-rolling	50	673	170	0.054	∞ (H_2/N_2)
Pd/HF[10]	ELP	3–4	703	100	0.136	1000 (H_2/N_2)
Pd–Ag/Al_2O_3[16]	ELP	2.2	623	200	1.0	260 (H_2/N_2)
This work	Complex method	5	773	100	0.333	∞ (H_2/He)
This work	Complex method	5	873	200	0.821	∞ (H_2/He)

[a] PSS is porous stainless steel tube, Al_2O_3 is Al_2O_3 tube, HF is α-Al_2O_3 hollow fiber, ELP is electroless plating, and MD is multi-dimension.

substrate was coated with polymer precursor layer containing Pd seeds, which is ultra smooth and gas tight. Then a thin and uniform Pd layer was pre-plated on the organic polymer coated substrate. Because the precursor polymer layer surface is very smooth and gas tight, there are no pinholes and penetration problems when the first Pd layer grows on it. The existence of Pd seeds in the ultra smooth and gas tight polymer layer leads to rapid and homogeneous plating. After that, the polymer precursor layer was almost completely removed by high temperature treatment in stagnant air. During the heating process a few small pores may be formed, which can be effectively removed by the second electroless plating. The most important thing is that the removal of the polymer layer can leave a small interstice between the Pd membrane and the porous substrate, which makes the Pd inner area increase greatly and decreases the shear stress between Pd layer and substrate. In addition, the scale of the small interstice can be easily controlled by the thickness of the polymer precursor layer. Therefore, using this method we can successfully prepare a thin and defect-free Pd-based membrane directly deposited on a big porous substrate without any interlayer and pore penetration which not only increases the gas permeation resistance but also decreases the membrane stability. Moreover, it can be used to prepare other thin supported inorganic membranes.

In conclusion, a thin and defect-free Pd-based membrane having a uniform thickness of 5 μm was directly coated onto big porous α-Al_2O_3 hollow fiber without any interlayer and pore penetration by a novel combined organic and inorganic method. The resulting small interstice between substrate layer and membrane layer can increase the hydrogen permeance and stability greatly.

Financial support from the Japan Society for the Promotion of Science (JSPS) is gratefully acknowledged. The authors thank Dr R. Kojima of NOK Corp. for providing the α-Al_2O_3 hollow fibers.

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