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Thin Pd membrane prepared on macroporous stainless steel tube filter by an *in-situ* multi-dimensional plating mechanism†

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The big surface pores of a porous stainless steel (PSS) tube filter with marked roughness were jammed with aluminium hydroxide gel by a combination of ultrasonic vibration and vacuum suction, then a thin dense Pd membrane (6 μm) was plated *in-situ* on this pre-jammed filter by a multi-dimensional plating mechanism; after recovering the substrate pores by high temperature treatment, higher H_2 permeance and complete H_2 selectivity were obtained.

The increasing demand for pure H_2 has catalyzed research in Pd membranes for production, separation or purification of H_2 in many fields such as petrochemicals, petroleum refining, and semiconductor processing, as well as in the area of new clean fuel for fuel cells and vehicles.[1,2] Moreover, in recent years, the application of Pd membrane reactors to H_2 related reactions has attracted great attention due to its industrial potential.[3–5] However, the key demands for industrialization, low investment as well as high H_2 permeance and permselectivity combined with good mechanical/thermal and long-term stability, have not been realized as yet.

Supported Pd membrane on PSS substrate has more potential compared with other Pd membrane configurations such as thick-wall Pd membrane, self-supported Pd membrane and supported Pd membrane on porous ceramic, vycor glass and silver or H_2 permeable metals.[6,7] But the big pores and marked roughness of the PSS support severely inhibit the preparation of thin dense Pd membrane.[8]

In order to prepare thin dense Pd membrane on macroporous substrates, researchers have introduced middle layers to decrease the surface pore size and the roughness.[8–10] Here, we developed a method to directly prepare thin dense Pd membrane on a macroporous tube with nominal particle retention size of 0.5 μm (Mott Metallurgical). The effective length, OD and ID are 70 mm, 9.5 mm and 7 mm, respectively. The surface pore size is 20–100 μm and the biggest roughness is 80 μm. An aluminium hydroxide sol of controlled particle size and viscidity was prepared from aluminium nitrate and ammonium carbonate. The tube was jammed with the sol under the conditions of ultrasonic vibration and vacuum suction for 1 h. Then the jamming was continued for another 1 h only with vacuum suction. After jamming, the water flux through the tube under 100 kPa pressure difference was measured to be almost zero, which implied that the jamming was almost complete under 0 kPa pressure difference (activating and plating conditions). The as-modified tube was activated *in-situ* by a commercial Pd catalyst solution (OPC-50 inducer and OPC-150 cryster) from Okuno Chemical Industries Co., Ltd. The mild electroless plating was carried out in a commercial Pd-plating bath (PALLA TOP) from the same company under mild conditions (pH value was 6–8, temperature was 303–318 K). Further Pd plating was performed continuously in the same kind of plating bath (but pH value was 5–6 and temperature was 323–343 K) for 3 h. The membrane thickness was evaluated by three methods. Firstly, the decrease of Pd concentration after plating was measured by ICP (ICPS-7000, Shimadzu). Combining with the pre-determined plating area, the membrane thickness could be obtained. Secondly, the mass increase of the tube filter after plating was measured. Together with the pre-determined plating area, the membrane thickness could be calculated. Thirdly, the smaller stainless steel sheet with designated big surface area and smaller mass was used as membrane thickness indicator. Through the mass increase and the exactly designated plating area of this indicator, the exact membrane thickness could be obtained. The Pd thickness results by these three methods are almost the same. The 6-μm Pd membrane was obtained. Before H_2 measurement, the temperature of the as-prepared membrane was increased to 773 K at the rate of 0.5 K min^{-1} in an Ar stream. Then the temperature was kept at 773 K for 3 h in a pure H_2 stream to recover the substrate pores.

The surface morphology of our membrane was characterized using a laser microscope (Keyence VK8500). Fig. 1(A) shows that the Pd was not only plated on the support wall, but also plated into the surface pores. The Pd membrane is almost dense, which is consistent with the complete H_2 selectivity. Fig. 1(B) shows that the roughness of the Pd membrane surface is about 20 μm, which is much larger than that of supported Pd membrane on porous ceramic, vycor glass or hollow fiber.[9,11] Roughness is related to effective Pd surface area, which has a big effect on the H_2 permeance of thin Pd membranes.[11]

For our membrane, the H_2 flux *versus* the pressure gradients at different temperatures are shown in Fig. 2. The H_2 flux increases rapidly with the increase of temperature and pressure gradients. At 823 K and 100 kPa pressure gradient the higher H_2 flux of 0.3 mol m^{-2} s^{-1} was obtained. Table 1 shows the comparative results for different Pd-based membranes. It is obvious that our membrane has better performance. From Fig. 2, it can also be seen that, at all the three temperatures, the H_2 flux is proportional to the H_2 pressure gradients (P_H–P_L, kPa). The exponent value of H_2 partial pressure which reflects the mechanism of H_2 transport is about 1, which greatly deviates from Sieverts' law.[12] This indicates that the surface reactions or the substrate diffusion takes up most of the permeation resistance. However, we have also measured the hydrogen flux under the same conditions for the pre-jammed substrate without Pd. When we obtain the same hydrogen permeation flux at the same operation temperature, the pressure difference is less than 4% of the pressure difference through the Pd composite membrane. At the same time, the same H_2 flux was

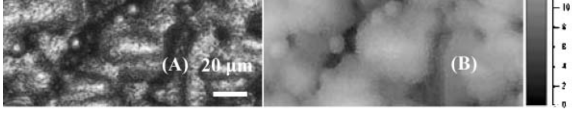

Fig. 1 Laser microscope images of the thin Pd membrane. (A) Surface image. (B) Simple high and low image.

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b4/b406975g/

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Table 1 Comparison of the permeation results for different palladium-based composite membranes

Membrane	Preparation method	Thickness/μm	Temperature/K	Driving force/kPa	H_2 flux/mol m^{-2} s^{-1}	Separation factor
Pd/SS[6]	ELP	19	773	100	0.083	1000
Pd/SS[16]	ELP	10	753	100	0.089	1000
Pd/Al_2O_3[3]	ELP	7–15	673	100	0.086–0.134	100–1000
Pd/HF[9]	ELP	3–4	703	100	0.136	1000
This work	MD-ELP	6	773	100	0.260	∞

SS is stainless steel tube; Al_2O_3 is Al_2O_3 tube; HF is Al_2O_3 hollow fiber; ELP is electroless plating; MD is multi-dimensional.

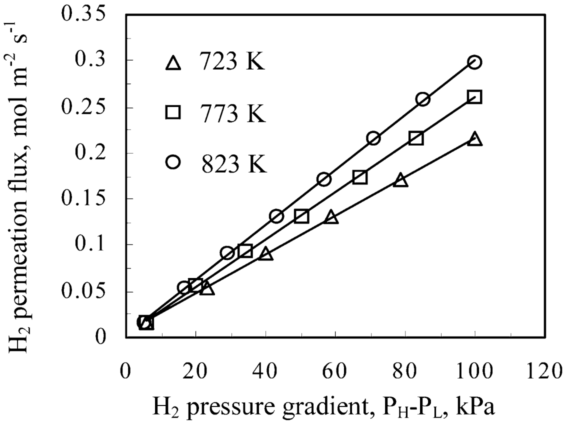

Fig. 2 The H_2 permeation flux of thin Pd membrane *versus* H_2 pressure gradients.

obtained for different permeation directions (from outside to inside or from inside to outside). These two results show clearly that the resistance of the support layer is negligibly small.[13] Therefore, the H_2 permeation process of our membrane is mainly controlled by surface reactions. Moreover, the activation energy for H_2 transport was calculated to be 16.7 kJ mol^{-1}. The higher activation energy than that of the bulk diffusion controlling process (10–12 kJ mol^{-1}) is similar to the value of the surface reactions controlling step.[9,14,15]

In the H_2 measurement process, the Ar leak is almost zero. After H_2 measurement, the membrane reactor was constructed for steam reforming of CH_4. Before reaction, He and N_2 were introduced to the reaction side and the sweep side, respectively. Until He pressure was increased to 300 kPa, we could not detect He in the sweep side by GC. During the reaction process, until the reaction pressure was increased to 500 kPa, we still could not detect CH_4, H_2O, CO, or CO_2 in the sweep side by GC. This result indicates that our membrane possesses complete H_2 selectivity under the experimental conditions and it is almost fully dense.

The better permeation performance resulted from the thin dense Pd layer, macroporous substrate and marked roughness. In the normal case, it is impossible to directly prepare thin dense Pd membrane on a macroporous support by the pore-cover plating mechanism,[6] which is shown in Fig. 3(A). It can be seen that Pd seeds can only be planted on the support wall. During the plating process, the Pd will grow from Pd seeds on the support wall. It will take a long time to span a big pore because the surface pore size is 20–100 μm. Moreover, the thickness is not very uniform. For this Pd membrane, not only is the H_2 flux lower due to the larger thickness, but also defects form easily in the thinner zone. The preparation mechanism of our Pd membrane is shown in Fig. 3(B). The big surface pores of the macroporous support are jammed by aluminium hydroxide sol before Pd plating. The water flux through this pre-jammed substrate under about 100 kPa pressure difference is about zero, which indicates that the activating solution and the plating solution cannot go through the substrate during the activating and plating process under about zero pressure difference. This also demonstrates that the macropores of the substrate have been jammed almost completely under the conditions of the activating and plating process. The Pd seeds are planted not only on the support wall, but also on the aluminium hydroxide particles inside pores. So the Pd will grow not only on the support wall, but also on the aluminium hydroxide particles inside the pores, which is a multi-dimensional plating mechanism. Therefore, by using this method we obtained a thinner dense Pd membrane on the almost completely jammed tube substrate. Before the H_2 measurement, the as-prepared membrane is treated under the designated conditions as mentioned above. During this process the original big pores of substrate are recovered by the great decrease (about 87%) of the volume of the aluminium hydroxide particles as shown in Fig. 3(C). But the thin Pd layer has not been affected. At the same time due to this process of a great decrease of the aluminium hydroxide particles volume, the inner surface area of the Pd membrane is also recovered, which is almost the same as the effective outside surface area. This is consistent with the result of the same H_2 flux for different permeation directions (from outside to inside or from inside to outside).

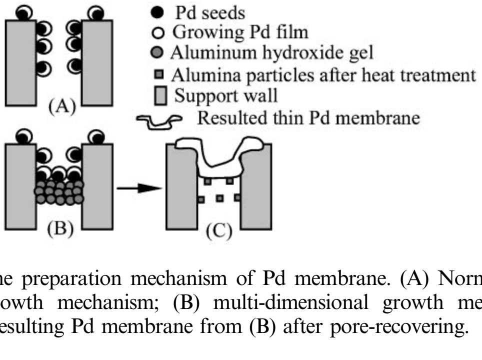

Fig. 3 The preparation mechanism of Pd membrane. (A) Normal pore-cover growth mechanism; (B) multi-dimensional growth mechanism; (C) the resulting Pd membrane from (B) after pore-recovering.

In conclusion, thin dense Pd membrane was directly prepared on a macroporous stainless steel tube filter by a multi-dimensional plating process. For this membrane the higher H_2 flux of 0.3 mol m^{-2} s^{-1} at 823 K and 100 kPa gradients was obtained.

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