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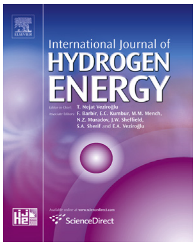

Silver coating on porous stainless steel substrate and preparation of H_2-permeable palladium membranes

Lei Wei, Jian Yu, Yan Huang[*]

State Key Laboratory of Materials-oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Xin-Mo-Fan Road 5, Nanjing 210009, PR China

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ABSTRACT

The H_2-permeable palladium membranes based on porous stainless steel (PSS) substrate are important for development of various hydrogen energy systems. To improve the surface of the PSS, a microporous silver layer was deposited successively by a coating with a suspension of silver powder in polyvinyl alcohol (PVA) solution, a heating under nitrogen at 500 °C for carbonization of PVA, an air treatment and a hydrogen reduction. The formation of carbon from PVA helps to maintain the porosity and integrity of the silver layer. After an activation of the resulting Ag/PSS surface through galvanic-cell reaction, palladium membranes with a thickness around 4 μm were successfully prepared by a suction-assisted electroless plating. SEM, EDS, metallography and porometry analyzes were conducted for material characterizations. The prepared Pd/Ag/PSS membrane is permeable and selective as compared with similar those reported in literature. The permeation tests were carried out at 350, 400, 450 and 500 °C for 48, 48, 48 and 60 h, respectively, and the membrane was found to be unstable at 500 °C due to the presence of pinholes. No significant intermetallic diffusion between the silver and palladium layers was observed.

1. Introduction

Palladium membranes (including Pd-based alloy ones) have attracted renewed attention, since the compact hydrogen separators based on H_2-permselective membranes are of key importance for various hydrogen energy systems [1–5]. Commercial palladium membranes are usually manufactured by cold rolling and have been mainly applied in purification of hydrogen and its isotopes, but they suffer from disadvantages such as high cost, weak mechanical strength and low H_2-permeance. Therefore, the interests are increasing in development of composite palladium membranes which consist of a thin palladium layer and a porous substrate [6,7]. Apart from the preparation process of the palladium layer, the selection of the substrate material is also important. For the convenience of membrane application, porous stainless steel (PSS) would be a most preferable substrate material owing to its good weldability, robust physical strength and cost effectiveness.

Conventional PSS often has a high surface roughness, large pore size and wide pore size distribution and cannot satisfy the requirement for the preparation of thin and defect-free Pd/PSS membranes [8,9]. As the working temperature of palladium membranes is often above 300 °C, the intermetallic diffusion between the palladium membrane and the PSS substrate is also a problem for membrane stability during long-term operation. A common strategy is to coat the PSS

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[*] *Corresponding author*. Tel.: +86 25 83172253.
E-mail address: huangy@njut.edu.cn (Y. Huang).

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surface with a microporous ceramic layer [8–14], which not only improves the substrate surface but also acts as an intermetallic diffusion barrier, but it is highly challenging to obtain a high-quality ceramic layer due to the great difference between a ceramics and a metal [8]. Because of the thermal expansion mismatching, the sandwiched ceramic layer in the Pd/Ceramics/PSS membrane might damage the palladium layer in case of frequent heat cycling. An oxide layer can be created throughout the outer and inner surface of the PSS by oxidation pretreatment, and such layer might be used as a barrier if it is resistant to the working condition of the palladium membrane (i.e., the hydrogen reduction at high temperature) [15,16].

Beside of the ceramic layer, a metallic layer can be also considered in improving the PSS surface, but the intermetallic diffusion problem should be avoided by selection of proper working condition of the palladium membrane. Gryaznov et al. [17] modify the PSS surface with a porous layer of tungsten through magnetron sputtering before preparation of Pd–Ru alloy membranes. Tong et al. [18] deposit a thin silver layer on PSS by electroplating and then fill the pores of the Ag/PSS with an Al_2O_3 sol, and they claim that the silver coating is essential in avoiding the intermetallic diffusion between PSS and palladium. Ayturk et al. [19] introduce a porous Pd/Ag intermediate layer on PSS by means of a “bi-metal multi-layer (BMML) deposition”. In this work, a microporous layer of silver is deposited on the PSS substrate, and palladium membranes are successfully prepared through a suction-assisted electroless plating. The permeation performances and thermal stabilities are investigated in detail.

2. Experimental

2.1. Preparation

PSS tubes (material, 316 L; o.d., 13 mm; i.d., 8 mm; length, 60 mm) with an asymmetric structure were employed as the substrate material, and they were supplied by GaoQ Funct. Mat. Co., Nanjing, China. Some silver powder (diameter, 100–200 nm) and polyvinyl alcohol (PVA) were added into the deionized water under stirring. The mixture was slightly heated to dissolve PVA, and a homogenous Ag–PVA suspension was obtained, which contains 3 and 5% of silver and PVA, respectively. The PSS tubes were dip-coated with the suspension and dried in the ambient air overnight. The coated PSS tubes were heated at 500 °C with a ramp of 0.5 °C/min under nitrogen for 2 h, and the Ag–C/PSS tubes were obtained due to the carbonization of PVA. They were further treated at 500 °C under the air and hydrogen each for 0.5 h, but a purge with nitrogen was carried out for 5 min before feeding of hydrogen. Based on the resulting Ag/PSS substrate material, the palladium membranes were prepared by a suction-assisted electroless plating process, which was described in [20]. Prior to the plating, the Ag/PSS substrate was activated by an immersion in a $PdCl_2$–HCl solution ($PdCl_2$, 0.2 g L^{-1}; HCl, 38%, 1 mL L^{-1}) for 5 min, followed by a cleaning with water. The plating bath was composed of $PdCl_2$ 2.5 g L^{-1}, $Na_2EDTA \cdot 2H_2O$ 70 g L^{-1} and $NH_3 \cdot H_2O$ 250 mL L^{-1}. The reducing agent was a $N_2H_4 \cdot H_2O$ (0.2 mol L^{-1}) solution.

2.2. Characterization

The pore size was measured on a GaoQ PSDA–20 porometer by bubble point method. The surface morphology was analyzed by scanning electron microscopy (SEM, FEI Quanta–200) and field emission SEM (Hitachi S–4800), and the latter was also used for energy dispersive spectroscopy (EDS) analysis. Cross-sectional analysis was performed with a metallographic microscope (LEICA DM–4000M), but the sample was encapsulated in epoxy resin, followed by grinding and polishing on a Buehler Phoenix Beta system. The permeation performances of one of the prepared Pd/Ag/PSS membranes were investigated with H_2/N_2 single-gas testing. The membrane was assembled in a testing cell and sealed with graphite gaskets [21]. An air-treatment was carried out at 350 °C for 2 h [22]. The hydrogen or nitrogen was fed to the shell side of the membrane, while the permeate side was always ambient. The hydrogen selectivity was defined as the ratio of H_2 and N_2 fluxes under the same condition.

3. Results and discussion

The photograph and SEM micrograph of the PSS material are demonstrated in Fig. 1(a). The surface of PSS is composed of sintered spherical stainless steel powder with a particle size of 4–10 μm. Although the average pore size as measured by bubble point method was around 0.5 μm, the pore mouths of the PSS as observed by SEM can be above 5 μm, and such a disagreement is because the bubble point method detects only the size of the pore-throat (i.e., the narrowest position of the pore channel). Since it is almost impossible to prepare a palladium membrane directly over such kind of PSS substrate material [23], a porous layer of silver was deposited to improve the PSS surface.

The PSS was coated with a Ag–PVA suspension at first, noting that the PVA is a common film-forming agent. Then, an important action that was taken in this work was to heat the Ag–PVA/PSS under inert atmosphere for carbonization of PVA, and the Ag–C/PSS was obtained. Finally, the Ag/PSS was prepared by an air treatment and a reduction. As found by our preliminary experiments, the resulting carbon in Ag–C/PSS acts as a template and helps to maintain the porosity and integrity of the silver layer of Ag/PSS. The Ag–C/PSS and Ag/PSS are exhibited in Fig. 1(b and c). The Ag–C/PSS looks black and lustrous as shown by its photograph, and no pores or cracks can be observed from its SEM micrograph. The Ag/PSS looks grey and smooth. The silver layer is continuous without significant defects, and the surface pore size as observed from SEM is 0.1–0.5 μm. The nitrogen permeance of Ag–C/PSS and Ag/PSS as tested at room temperature is 0.01 and 0.87 $m^3\ m^{-2}\ h^{-1}\ kPa^{-1}$, respectively.

Electroless plating is well recognized as an effective approach for preparation of palladium membranes. Although the Ag/PSS surface itself is conductive and can directly catalyze the reduction of palladium ions during electroless plating, an extra activation was still conducted to seed palladium nuclei as catalyst and ensure the homogenous deposition of palladium. For such an activation, the $SnCl_2/PdCl_2$ process is conventional, but it has disadvantages such as tin