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Electroless plating of Pd after shielding the bottom of planar porous stainless steel for a highly stable hydrogen selective membrane

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ABSTRACT

This study demonstrates that thermally stable palladium membranes can be electrolessly plated on ZrO_2 modified planar porous stainless steel (PSS) with EDTA-free bath following a palmitic acid treatment. Prior to elctrroless plating of palladium with EDTA-free bath, the bottom of the ceramic-modified planar porous stainless steel (PSS) was shielded by a palmitic acid prior to palladium plating to prevent the diffusion of the plating solution through the bottom of the substrate that causes palladium plating in the pores of the PSS. The hydrogen permeation flux and the nitrogen leakage were monitored for an extended period of time at a pressure difference of 100 kPa and 873 K and showed that the palmitic acid-treatment provided membrane stability at high-temperature.

1. Introduction

In Pd based membranes, the composite structures can offer a reduction in material cost and a high hydrogen permeation rate because an ultra-thin membrane film can be prepared. The materials that have been commercially used for supports are ceramics, glass and stainless steel [1,2]. Recently, Hastelloy [3], Inconel [4] and nickel [5,6] have been reported. From the viewpoint of a practical application, porous metal supports are sealed more readily into a commercial unit. However, an atomic interdiffusion of metals between the thin Pd alloy layer and the metals occurs during high temperature processing. To inhibit the atomic interdiffusion, a ceramic layer is introduced as a diffusion barrier, such as Al_2O_3 [3,7,8], ZrO_2 [5,9], yttria-stabilized zirconia (YSZ) [9], TiO_2 [9], WO_3 [10], Cr_2O_3 [11], CeO_2 [6] and TiN [12].

Depending on their geometry, the membrane can be subdivided into a tubular, hollow fiber, spiral wound and flat sheet (planar) geometry. In metallically dense membranes for hydrogen separation, a tubular and planar geometry are common. Tubular membranes are easy to clean and provide suitable hydrodynamic control, but they require a relatively high volume per membrane area unit and present high costs. Planar membranes are susceptible to plugging due to a flow stagnation point, are difficult to clean and are expensive. However, they offer higher membrane surface/volume ratios than tubular membranes [13]. Furthermore, planar membranes provide easy module configuration to reduce the concentration polarization effect. Recently, we effectively reduced the concentration polarization by reducing the space distance between the surface of the membrane and the cover plate in the planar membrane module [14].

The common methods for preparing a Pd-based composite membrane are sputtering, chemical vapor deposition (CVD), electroplating, spray pyrolysis and electroless plating (ELP) [1,2]. The ELP method (i.e., the so-called auto catalytic deposition) has a number of advantages over other methods, including the uniformity of deposits on complex shapes, the hardness of the deposits, low cost and simplicity [15]. Lu et al. [16] reported that membranes that were produced using ELP have the highest permeabilities compared with other methods, such as CVD and sputtering.

Long-term thermal stability is one of the essential issues in the membrane industries, especially membrane reformer. Some literatures reported that Pd based membranes prepared by ELP on various PSS substrates were highly stable at high-temperature and most of them showed the stability at 723–773 K or for <1 day at 873–923 [3,17–21]. Most ELP studies have used EDTA salt because it increases the stability of the bath and assists in controlling the plating process at different temperatures. However, the EDTA salt causes low purity in the palladium layer due to the incorporation of the EDTA complex within the metal deposit and the contamination

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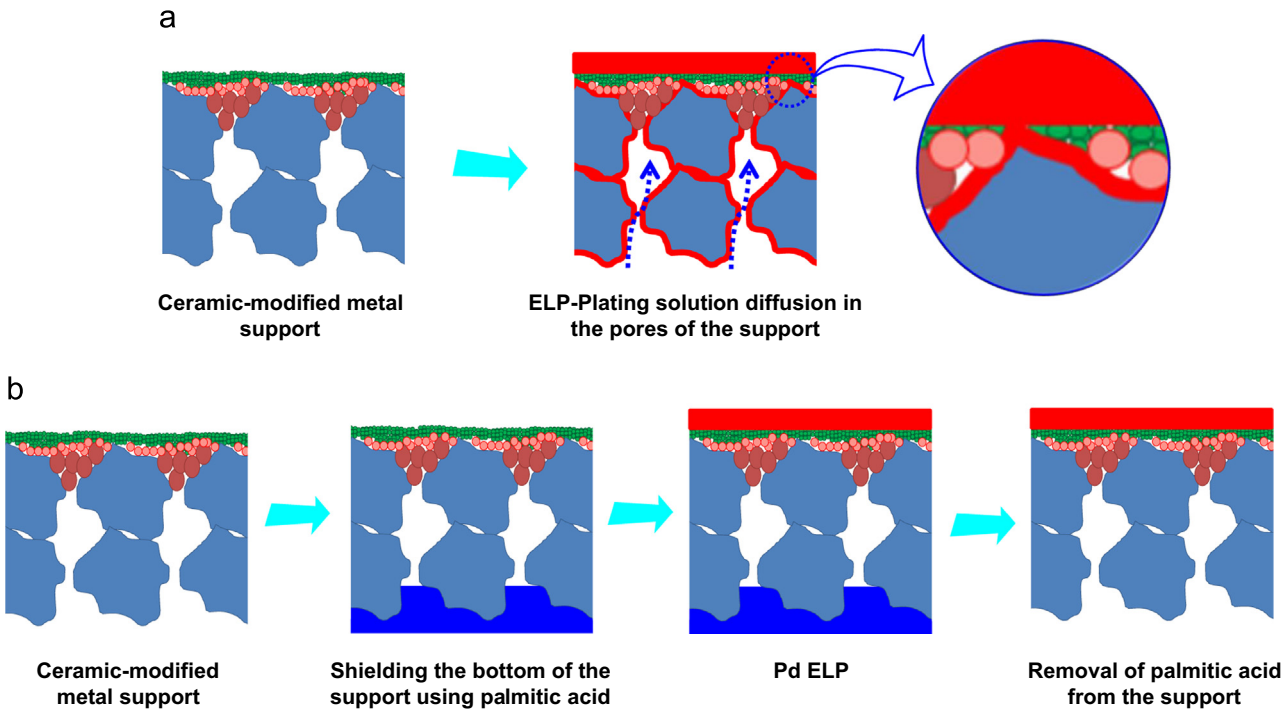

Fig. 1. Conventional (a) and palmitic acid treatment method (b) electroless plating in a Pd composite membrane deposited on ZrO_2 modified planar PSS.

of carbon [22–24]. Recently, the University of British Columbia (UBC) developed an EDTA-free ELP method, which was performed at room temperature [3,7]. The room temperature ELP method has several advantages, including very high selectivity, stability, favorable energy efficiency and simplicity.

In spite of several advantages of EDTA-free ELP method, there is a drawback to overcome. When using planar substrates in EDTA-free ELP method, the plating solution diffuses into the bottom of the substrate, and palladium is plated on the surface of the metal grain that composes the substrate because of low stability of plating solution (see Fig. 1(a)). Occasionally, the palladium growth on the surface of the metal grain connects the membrane layer with the metal substrate and causes an intermetallic diffusion between the two components during high temperature processing. Moreover, the palladium plating on the surface of the metal grain of the substrate causes palladium ion waste in the plating solution.

This study was focused on the thermal stability problem typically observed in Pd-based composite membrane deposited on PSS using EDTA-free method and performed to avoid palladium deposition in the pores of a planar metal support during electroless palladium plating using an EDTA-free bath. The bottom of the ceramic-modified planar porous stainless steel (PSS) was shielded by palmitic acid prior to palladium plating (see Fig. 1(b)). Following palladium plating, the palmitic acid was removed from the bottom of the support using heat. Thermal stability test was carried out at 873 K, i.e. the temperature of typical Steam Methane Reforming (SMR) membrane reactor, for ~170 h. The palmitic acid-treated membrane and the conventional membrane were compared with the SEM analysis, the EDX analysis of the membrane surface, the EDX line scanning of the membrane cross-section and the membrane stability test at 873 K.

2. Experimental

2.1. Substrate preparation

Palladium membranes were synthesized on pre-treated porous stainless steel (PSS) discs with a 50.8-mm diameter and a 1.2-mm thickness (Mott, 0.5 μm grade). The PSS was pretreated using the method listed below.

(1) Heat treatment of the PSS under air at 650 °C for 2 h.
(2) 5-μm ZrO_2 powder filling.
(3) Heat treatment under air at 650 °C for 2 h.
(4) Sub-micron ZrO_2 powder filling.
(5) Heat treatment under air at 650 °C for 2 h.
(6) Nano-size ZrO_2 powder filling.
(7) Heat treatment under air at 650 °C for 2 h.
(8) Diffusion barrier ZrO_2 coating followed by Pd seeding and DC magnetron sputtering.

To fill the entrance pores of the PSS, three different sizes of ZrO_2 powder (i.e., 5 μm, sub-micron and nano-size (<100 nm)) were added into the acetone at 2.5 wt% and were ultrasonically dispersed for 5 min. To ensure that the ZrO_2 particles filled the entrance pores of the PSS, a vacuum was applied to the other side of the PSS. The details of the powder filling method were shown in a previous study [25]. The surface roughness between the fresh PSS and the modified PSS was compared using a color confocal microscope (Lazertec, Optics H1200). To prevent an intermetallic diffusion barrier, a ZrO_2 barrier was sputtered on the surface of the modified PSS using a DC magnetron sputtering system. The thickness, diameter and purity of the ZrO_2 target were 3.175 mm, 50.8 mm and 99.995 wt%, respectively. After the ZrO_2 sputtering, Pd was seeded in the same sputter using a 99.995 wt% Pd target. Before deposition, the sputtering chamber was evacuated to 2.0×10^{-6} Torr and then filled with high-purity argon. During the sputtering of ZrO_2 and Pd, the substrate was maintained at ~150 mm from the sputtering gun, and the sputtering chamber was maintained at 1 mTorr in high-purity argon.

2.2. Electroless Pd plating

Prior to electroless Pd plating, palmitic acid was melted at ~343 K and applied on the bottom of the prepared substrate using a brush. The liquefied palmitic acid was solidified easily at room