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Preparation of palladium membrane by bio-membrane assisted electroless plating for hydrogen separation

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ABSTRACT

Palladium membrane was prepared on the inner surface of alumina tube by bio-membrane assisted electroless plating combined with osmosis method (BELP). In this preparation technique, an egg-shell film not only served as a semipermeable membrane to form osmotic system for preparing palladium membrane, but also acted as a protection layer to prevent the contamination of the palladium membrane from the osmotic solution. Moreover, the plating solution was circulated through the tube side to promote the mass transfer on the solid–liquid interface between the plating surface and the solution. The detailed depositing process of the palladium membrane was studied by scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDXS). Both long term operation and temperature cycling test carried out for hydrogen and nitrogen permeation confirmed that the palladium membrane was stable.

Introduction

Palladium-based membranes have been attracting much considerable attention for applications in separation and purification of hydrogen due to their high permeability and unique selectivity for hydrogen [1–7]. However, commercial palladium membranes are thick, resulting in consuming more precious palladium and losing hydrogen permeance. To solve these problems, current developments tend to employ composite membranes in which the palladium membrane is deposited as a thin film onto porous support, i.e., porous stainless steel, ceramics and glass, giving the membrane high permeability, mechanical strength and thermal stability.

There are numerous methods for fabricating palladium composite membranes including sputtering [8,9], electroplating [10], chemical vapor deposition [11,12], photocatalytic deposition [13,14] and electroless plating [15–17]. Among these various methods, electroless plating is a generally preferred technique for depositing palladium membranes

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due to its many advantages, such as inexpensive and simple, in particular for deposition on conducting and non-conducting substrates with complex shapes. Most of studies focused on fabrication of palladium membranes on outer surface of tubular substrates. However, the palladium membrane is prone to be polluted and scraped, which affects its hydrogen permeability and service life in industrial applications, such as steam reforming [18–21] and fuel cell [22,23].

A good solution is to prepare palladium membrane on the inner surface of tubular substrates. However, to date, there have been few literatures addressing this issue on palladium membrane [24]. This is mainly caused by the serious aggregation of the deposited palladium particles on the inner wall, which leads to large grain formation and some pinholes. Electroless plating combined with osmosis technique (OELP) was developed to obtain thin and dense palladium membranes [25–29]. During the plating process, osmosis occurred in the plating system depends on two necessary conditions. First, the support served as a semi-permeable membrane should have smaller pore size, which allows only water molecules to move freely through the aperture of the substrate. Second, concentrations of solutions in both sides of the substrate are different in plating system, in which water molecules can transfer from one side of a plating solution with lower concentration to the other side of an osmotic solution with higher concentration based on the concentration difference. Owing to the osmotic effect, the osmotic flux carries Pd^{2+} species from the plating solution to the targeted substrate surface, which promotes the further deposition of palladium. The studies performed by Yeung et al. [25], Souleimanova et al. [26–28] and Li et al. [29] have shown that the osmosis process can enhance interaction of palladium layer with the substrate, which makes the films more uniform and have finer microstructure.

Although great progress has been made, there are still some problems existed in the OELP method to be solved. In the preparation system, osmotic solution with high concentration has to be employed to generate osmotic pressure. Thus, this makes some solutes (i.e. NaCl, $CaCl_2$, sucrose and polyethylene glycol) difficult to be completely cleaned away from the substrates after plating palladium. The remainder will pollute the palladium membranes and inhibit hydrogen surface dissolution and transport. This is an important factor for the application of OELP method. Moreover, support morphology is also limited for serving as semipermeable membrane to constitute osmotic system. Therefore, the OELP technique remains challenging for preparing palladium membrane.

This work presents a novel method of preparing a thin and dense palladium membrane on an inner surface of alumina tube by bio-membrane assisted electroless plating combined with osmosis method (BELP), in which a semipermeable egg-shell film was applied in the plating system, serving as a protection layer to prevent the contamination of the palladium membrane from the osmotic solution. The palladium membrane microstructure, permeation performance and stability were investigated in details.

Experimental

Membrane support

Porous alumina tubes (o.d., 12 mm; i.d., 8 mm; length, 75 mm; pore size of inner wall, 200 nm; pore size of outer wall, 2 μm) with an asymmetric structure were used as the substrate, and they were purchased from Foshan Ceramics Research Institute of China. To remove the possible contaminants on the substrate surface and in the pores, the tubes were washed successively with dilute HCl and NaOH, deionized water and ethanol in an ultrasonic cleaner. After drying overnight in oven at 393 K, the ends of alumina tubes were sealed with glass glaze, leaving a porous length of 30 mm for hydrogen permeation.

Fabrication of bio-membrane

A fresh egg was knocked to get a small hole with a diameter of 5 mm, after spilling the yolk and egg white and rinsing with deionized water, it was immersed in 10% (v/v) HCl (37 wt.%) for 3–5 min to make the egg-shell film separated from the outer calcified shell [30,31]. Afterwards, the bio-membrane was cleaned thoroughly using deionized water for several times, and then it was restored in deionized water for preparation of palladium membrane as semipermeable membrane.

Deposition of palladium membrane by BELP

Prior to electroless plating, the activation procedure was performed at room temperature, consisting of a two-step immersion sequence in an acidic $SnCl_2$ solution (2 g L^{-1}), followed by an acidic $PdCl_2$ solution (0.2 g L^{-1}). The procedure was repeated 5 times to obtain uniform activation for the support. Thereafter, the outer wall of activated substrate was wrapped with the egg-shell film, which acted as a semi-permeable membrane to form osmotic system in the following electroless plating. During the coating of the bio-membrane on the activated support, the joint between the bio-membrane and the support was sealed with Teflon membrane. As depicted schematically in Fig. 1, the support coated with the egg-shell film was set in our home-made

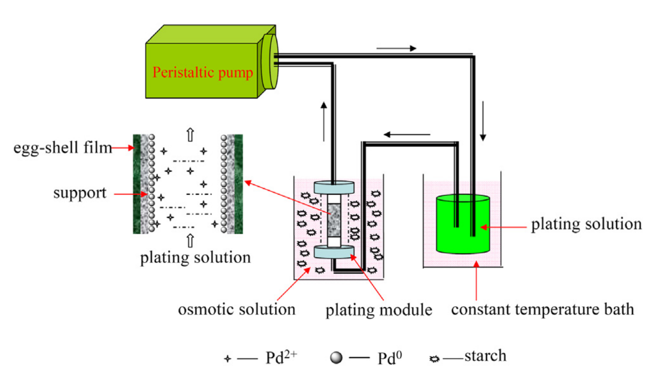

Fig. 1 – Fabrication scheme for palladium membranes with BELP method.