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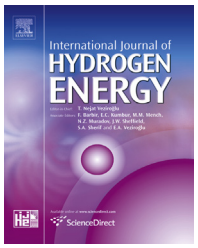

Toward extensive application of Pd/ceramic membranes for hydrogen separation: A case study on membrane recycling and reuse in the fabrication of new membranes

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ABSTRACT

The increasing applications of hydrogen energy greatly promote the development of composite palladium membranes, which are ideal for hydrogen purification because of their high permeability, excellent permselectivity and easy modulation. However, these membranes are still associated with problems such as high cost and limited operating life. This work investigates membrane recycling and reuse as a solution to these problems. Pd/Al_2O_3 membranes were prepared by electroless plating. The recycling of palladium was achieved by treating it with HNO_3 and HCl–H_2O_2 agents. Adequate results were achieved using an agent composed of 2 mol/L HCl and 1 mol/L H_2O_2. The recycled palladium can be utilized in a new plating bath, while the Al_2O_3 substrate remaining after palladium recycling can be reused as the substrate material for the preparation of new membranes. The surface morphology, thickness and permeation performances of the recycled membranes, as characterized by scanning electron microscopy, metallographic microscopy and permeation tests, are similar to those of the original palladium membranes. It can be concluded that the recycling and reuse of the Pd/Al_2O_3 membranes are successful and may provide a solution to the current key problems associated with the application of composite palladium membranes.

Introduction

Hydrogen energy systems place a high demand on the compactness of the hydrogen generators, which usually comprise a hydrogen producer and a hydrogen purifier. Among various technologies for hydrogen separation, the membrane approach is one of the best choices because of its simplicity and compactness. Palladium membranes (including those composed of palladium-alloys) have been commercially applied in hydrogen separation and purification for about half a century, and they are usually manufactured by cold rolling [1–3]. However, a number of disadvantages, such as low permeance and poor physical strength have greatly

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limited their applications [4,5]. One solution is to deposit palladium membranes on a porous substrate to form composite membranes. In this case, the membrane thickness can be reduced to several microns, and in return, the hydrogen permeance can be increased by up to one order of magnitude [6–8]. In addition, the enhanced membrane mechanical strength greatly facilitates membrane module construction. However, one challenge against the industrial application of these composite palladium membranes is their limited operating life [9–11]. For example, depending on the required hydrogen purity, a membrane may have to be replaced when 0.1 or 0.01 percent of its area is broken, because the membrane selectivity is highly sensitive to the membrane defects.

To avoid hydrogen embrittlement, enhance poison (such as CO) resistance and maintain the hydrogen permeability, palladium membranes are often operated at temperatures above 300 °C [12–14]. The lifetime of Pd membranes is largely dependent on the operating conditions. When palladium membranes are used as membrane reactors for reactions such as hydrogen production, hydrogenation or dehydrogenation, they may have to work under severe conditions. During long-term operation, an increasing number of pinholes will appear as the running time increases [15–19]. Once membrane defects accumulate to a certain degree, the purity of the hydrogen at the permeate side will fall below the required value, ending the life of the membrane. Principally, the life of a composite palladium membrane is shorter than that of a conventional self-supported membrane. This situation creates a high demand for cost reduction in the production of composite membranes. This can be carried out by improving the fabrication process [20,21] and by recycling and reusing the membrane [22]. In addition to palladium, the substrate material is often also expensive because its quality (particularly its surface quality) plays a key role in membrane fabrication and performance [6,23,24]. Therefore, both the membrane layer and the substrate material should be recycled and reused in the preparation of new membranes.

Because Pd/Al_2O_3 composite membranes, which are often fabricated by deposition of a palladium layer through electroless plating on a porous Al_2O_3 substrate, are the most common type [6], the present work investigates the possibility and feasibility of the preparation of new membranes by recycling and reusing old membranes.

Experimental

Membrane preparation

The original substrate material employed in this work is porous Al_2O_3 (o.d., 12 mm; i.d., 8 mm; supplied by Jiusi Co., Nanjing, China) which has an asymmetric structure and an average pore size of 0.2 μm. All the Pd/Al_2O_3 membranes in this work were prepared by electroless plating at 30 °C with plating baths made from either $PdCl_2$ or the recycled palladium. The former is composed of $PdCl_2$ (2.5 g/L), $Na_2EDTA{\cdot}2H_2O$ (70 g/L) and $NH_3{\cdot}H_2O$ (28%, 250 ml/L). The reducing agent is a 0.2 mol/L hydrazine solution. Before plating, the substrates were activated with a conventional $SnCl_2/PdCl_2$ method [25]. They were alternately immersed in a $SnCl_2$ solution ($SnCl_2{\cdot}2H_2O$, 5 g/L; HCl, 1 ml/L) and in a $PdCl_2$ solution ($PdCl_2$, 0.2 g/L; HCl, 1 ml/L) for about 10 min at 40 °C, but each immersion was followed by a rinse with deionized water. The above $SnCl_2/PdCl_2$ treatment was conducted for 4 times. During the typical electroless plating, an amount of 125 ml plating bath was used for a 75-mm-long membrane, and the whole plating time was about 15 h. The resulting membranes were cleaned with hot water and dried overnight at 120 °C.

Palladium recycling and recovery is a well-established industry (because palladium is a precious metal) with a variety of recycling and recovery processes [26–29]. The easiest way to recycle and recover palladium membranes is to dissolve the palladium layer with a chemical agent. To dissolve the palladium layer of the Pd/Al_2O_3 membranes, we used HNO_3 or HCl solutions with concentrations of 2, 4, 6 and 8 mol/L as the dissolving agents, but each HCl solution contains 1 mol/L H_2O_2, which acts as an oxidant to help the dissolving of palladium. Each time, a Pd/Al_2O_3 membrane was wetted with water and then soaked in 6 ml of a solution of HNO_3 or HCl at 70 °C for 2 h. The plating bath based on the recycled palladium will be described later, but the electroless plating process is the same.

Characterization

The pore size distribution of the Al_2O_3 substrate was analyzed with a PSDA-20 porometer (GaoQ Funct. Mater. Co., Nanjing, China) based on the bubble-point (also known as "capillary flow") method [30]. The surface morphologies were studied by scanning electron microscopy (SEM, FEI Quanta-200). For cross-sectional analysis through metallographic microscopy (Leica, DM-4000M), the samples were encapsulated with an epoxy resin and then treated with a Buehler Phoenix Beta grinder-polisher.

The membrane permeation performances were tested by both H_2/N_2 single gas and H_2–N_2 mixing gas methods [9,31]. The membranes were assembled in a compact testing cell and sealed with graphite gaskets [32], giving an effective permeation area of 18.5 cm^2. Before testing, each membrane was pretreated at 350 °C in air for 2 h, followed by a purge with nitrogen for 5 min. The permeate side (i.e., the tube side) of the membranes was always under ambient conditions. During the single gas test, the fluxes of pure nitrogen and hydrogen were measured as a function of pressures at the retentate side (i.e., the shell side), and the membrane selectivity was defined as the ratio of H_2 flux vs. N_2 flux at the same temperature and pressure. During the mixing gas tests, the feed gas was changed with a mixture of H_2 and N_2 with $H_2/N_2 = 5{:}1$, and the feed rate is 0–1.6 L/min. The hydrogen recovery rate was maintained at 60%. The nitrogen concentration in the hydrogen permeated through the membranes was analyzed with an online gas chromatography. The membrane selectivity during mixing gas tests is defined as the H_2/N_2 ratio in permeated hydrogen versus that in the feed gas.

Results and discussion

Palladium recycling

As a first step, several Pd/Al_2O_3 membrane samples with a length of 25 mm were fabricated. The photographs, surface