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Article

Bifunctional palladium composite membrane for hydrogen separation and catalytic CO methanation

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ABSTRACT

NiO was introduced into the porous Al_2O_3 substrate by impregnation, and the resulting $\text{NiO}/\text{Al}_2\text{O}_3$ was coated with the lead of a 2B pencil to modify its surface. A palladium layer with a thickness of 5 μm was deposited by electroless plating on the Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ substrate, and a Pd/Pencil/ $\text{Ni}/\text{Al}_2\text{O}_3$ membrane was obtained after reduction with hydrogen. For reference, a Ni-free Pd/Pencil/ Al_2O_3 membrane was also fabricated. The surface and cross-sectional morphologies of the membranes were studied by scanning electron microscopy and metallographic microscopy. The hydrogen permeation kinetics was investigated by single gas tests, and the hydrogen separation performances of the Pd/Pencil/ Al_2O_3 and Pd/Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ membranes were tested with a hydrogen feed composed of H_2 77.8%, CO 5.2%, CO_2 13.5%, and CH_4 3.5%. The Ni-free Pd/Pencil/ Al_2O_3 membrane only shows function of hydrogen separation, while the Pd/Pencil/ $\text{Ni}/\text{Al}_2\text{O}_3$ is also catalytically effective for methanation of CO and CO_2 in hydrogen, forming a bifunctional palladium membrane concept. Since the amount of CO and CO_2 in the hydrogen after membrane separation is very low, the consumption of hydrogen by the methanation reactions is negligible. The bifunctional membrane is promising for proton exchange membrane fuel cells because the catalytic methanation treatment solves the CO poisoning problem of the fuel cell electrodes and consequently allows the palladium membrane to tolerate more membrane defects and to achieve longer life.

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1. Introduction

Being different from the hydrogen production for industrial applications, that for hydrogen energy utilizations places a high demand on the miniaturization and portability of the hydrogen generation system, and a key unit of which is the hydrogen separator. Among various hydrogen separation processes, the membrane technology is of great advantage. Proton exchange membrane (PEM) fuel cells are the most common hydrogen-fueled ones [1,2]. Their anode contains a platinum catalyst, which is able to oxidize hydrogen to water at room tempera-

ture and release the electric power, but this catalyst requires a very high purity of hydrogen. Currently, most of the hydrogen is produced by steam reforming of fossil fuels, and it unavoidably contains a small amount of CO. Since CO can easily poison the platinum catalyst of the PEM fuel cell anode, the CO content in the hydrogen fuel has to be controlled to below 0.001% [3,4], and this is highly challenging for the membrane selectivity. A number of hydrogen separation membranes have been reported, but palladium and palladium-alloy membranes are preferred because they have high hydrogen permeability and the best permselectivity and can reject any other gas. On the

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other hand, it is of great interest to eliminate the CO in the hydrogen fuel. Apart from the membrane technology [5,6], catalytic oxidation [7,8] or methanation of CO [9,10] can be an alternative. The catalytic oxidation route needs the introduction of appropriate amount of oxygen and should convert CO to CO₂ without the oxidation of hydrogen, and the catalyst selectivity is of key importance. Catalytic methanation converts CO into CH₄ through catalytic hydrogenation. In addition to CO, the industrial hydrogen often contains CO₂, which can also be converted during methanation. Since the methanation of each mole of CO or CO₂ will need 3 or 4 mol hydrogen, this process is not applicable for the hydrogen feed with a high amount of CO and CO₂.

Commercial palladium alloy membranes are fabricated by cold rolling, and their thickness can be as thick as 50 μm or higher. Their disadvantages such as high cost, low hydrogen permeance, and poor mechanical strength greatly limited their applications. A significant improvement can be achieved by the use of composite membranes, i.e., very thin membranes supported on porous materials, and they can be one order of magnitude thinner than the conventional ones. However, the stability of composite Pd membranes is the key factor that limits their industrial applications. During long term membrane operation, pinholes will gradually appear and lead to a decrease in hydrogen purity. Once the CO concentration exceeds the level acceptable for the PEM fuel cells, the life of the Pd membranes is over. Since the PEM fuel cells are so sensitive to CO, the lifetime of the composite Pd membranes eventually becomes a key problem. Based on the characteristics of the methanation and membrane separation approaches, we invented a kind of bifunctional membranes [11], i.e., the Pd membranes with a Ni catalyst supported on their porous substrate material, so that both functions of hydrogen separation and CO methanation are integrated. On one hand, the catalytic methanation eases the strict requirement on the CO leakage through the Pd membranes and equivalently prolongs the membrane life. On the other hand, the contents of CO and CO₂ in the hydrogen after membrane separation are extremely low, and the hydrogen consumption will be negligible if the methanation is conducted thereafter.

In this work, a bifunctional Pd/Pencil/Ni/Al₂O₃ membrane with the functions of hydrogen separation and CO methanation was prepared, and its hydrogen separation performance was compared with that of the Ni-free Pd/Pencil/Al₂O₃ membrane.

2. Experimental

2.1. Membrane preparation

2.1.1. NiO deposition on Al₂O₃ substrate

Conventional porous Al₂O₃ ceramic tubes (o.d., 13 mm; i.d., 8 mm; length, 75 mm) with a symmetric structure were employed as the substrate material. They were cleaned with a hot solution of a commercial detergent, rinsed repeatedly with deionized water, and finally dried at 120 °C overnight.

NiO/Al₂O₃ was prepared by impregnation. The Al₂O₃ substrate was immersed in a Ni(NO₃)₂ solution (0.25 mol/L) for 10

h, then dried at 120 °C for 12 h, and finally calcined at 450 °C for 3 h. The NiO content as measured by weight gain was 3.6%, which amounts to a nickel content of 2.8%.

2.1.2. Substrate surface modification

The Al₂O₃ and NiO/Al₂O₃ surfaces were modified by means of pencil coating [12,13], which was carried out by scraping with a conventional 2B pencil so that a uniform and continuous coating layer can be created. The modified substrates were calcined at 450 °C for 3 h to burn off oil contaminants, resulting Pencil/Al₂O₃ and Pencil/NiO/Al₂O₃.

2.1.3. Electroless plating [14]

Before plating, the Pencil/Al₂O₃ and Pencil/NiO/Al₂O₃ were activated with the SnCl₂/PdCl₂ method. The sensitization and activation reagents were composed of 5 g/L SnCl₂ and 0.2 g/L PdCl₂, respectively, and both of reagents also contain 1 ml/L concentrated HCl. The electroless plating was carried out at 30 °C. The plating bath was composed of 5 g/L PdCl₂, 70 g/L Na₂EDTA, and 250 mL/L NH₃·H₂O (28%), and the reducing agent was a hydrazine solution (0.2 mol/L). The thickness of the Pd membranes was controlled by the volume of the plating bath, and it would be 5 μm if there was no loss of palladium.

2.2. Characterization and permeation tests

The pore size of the Al₂O₃ substrate was measured with a porometer (GaoQ PSDA-20) through a bubble-point (also known as gas-liquid displacement or capillary flow) method [15]. The surface morphology was studied by scanning electron microscopy (SEM, FEI Quanta-200). The cross-section of the Pd membranes was observed with a metallographic microscope (Leica DM-4000M), but the specimen were encapsulated with epoxy resin and pretreated on a grinder-polisher (Buehler Phenix Beta) before analysis.

The palladium membrane was assembled in a module (GaoQ PM-201S). The permeation kinetics was studied by the single gas method, and the practical hydrogen separation performance was tested with a gas mixture (H₂ 77.8%, CO 5.2%, CO₂ 13.5%, and CH₄ 3.5%). The pressure at the shell side of the membrane was controllable, while the pressure at the tube side of the membrane was always ambient. During testing, the NiO supported on the Al₂O₃ substrate was reduced in situ into the metallic nickel catalyst. The permeated hydrogen was analyzed with an online gas chromatograph (Shimadzu-2014).

3. Results and discussion

3.1. Membrane morphology

Porous Al₂O₃ is the most common substrate material for palladium membranes, but in this work it was also used as a support of the methanation catalyst. The porometry results indicate that the largest and the average pore sizes of the porous Al₂O₃ substrate are 1.5 and 3.7 μm, respectively. As reported in the literature, the substrate materials for Pd membranes often have an average pore size below 0.2 μm, and they

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