Fabrication of Supported Palladium Membrane for Membrane Reformer

Shigeyuki Uemiya*, Shogo Mishima**, Ikumi Miyazaki**, Ryo Yoshiie*,
Hiroshi Moritomi**, and Makoto Nishimura*

*Department of Human and Information Systems, Faculty of Engineering, Gifu University
**Environmental and Renewable Energy Systems Division, Graduate School of Engineering, Gifu University
Yanagido 1-1, Gifu 501-1193, Japan
Fax: 81-(0)58-293-2583, e-mail: uemiya@cc.gifu-u.ac.jp

A supported palladium membrane for hydrogen separation was fabricated by an electroless-plating technique. The fabrication time required for a dense and thin palladium film supported on a porous alumina having a mean pore size of 200 nm was shortened by the improvement of the surface activation procedure before the electroless plating. A dense palladium film with a thickness of 3.9 µm was fabricated by a 1-h electroless plating. The resulting membrane gave both excellent hydrogen permeance and permselectivity, applicable to a membrane reformer for PEFC. Hydrogen production via the steam reforming of n-butane was conducted using a membrane reformer incorporated with the supported palladium membrane having a different palladium thickness of 3.9 or 10.2 µm. The hydrogen yield increased with the decreasing thickness of the palladium film. Carbon monoxide, which may cause a serious problem for the platinum electrode of a PEFC, was hardly detected in a gas stream that permeated through the membrane.
Key words: electroless plating, hydrogen, membrane reformer, palladium, steam reforming

1. INTRODUCTION

A membrane reformer, which has the simultaneous functions of both the reaction and separation of hydrogen in one unit, has been proposed for producing pure hydrogen for a polymer electrolyte fuel cell (PEFC) [1]. Development of a novel hydrogen permeable membrane with an excellent hydrogen permeance and permselectivity as well as an active reforming catalyst is required for the realization and commercialization of the membrane reformer [2, 3].

Uemiya et al. reported such an application in a hydrogen permeable membrane reactor, in which the water gas shift reaction [4], the steam reforming of methane [5], and dehydrocyclization of propane [6] occurred. Therefore, it has been experimentally demonstrated that the product yields were dependent on the hydrogen permeance of the membranes used. They proposed the supported palladium and palladium-alloy membranes prepared by the electroless plating technique [7, 8]. The rate of palladium electroless plating was as low as 1-2 µm h⁻¹, and hence, at least a 10-hour electroless plating was required for the fabrication of the membrane having a thickness of 20 µm. In this paper, we describe an improved technique in order to shorten the fabrication time, and moreover, the resulting membranes with different thicknesses were used as a membrane reformer to investigate the effect of the hydrogen permeance of the membranes used on the hydrogen yield in the steam reforming of butane, which is one of the main components of liquefied petroleum gas (LPG).

2. EXPERIMENTAL

2.1 Membrane fabrication

A porous alumina tube with an asymmetric structure (o.d., 10 mm, i.d. 7 mm; mean pore size of effective layer, 0.2 µm) was used as a supporting material for a thin palladium film formed by the electroless plating technique. First, the tube was cleaned in an ultrasonic washing vessel. The surface of the tube was then activated and catalyzed by a conventional two step activation procedure using stannous chloride and palladium chloride aqueous solutions. This surface activation procedure usually consisted of the repeated immersion into a $SnCl_2$ aqueous solution ($SnCl_2$ 1.0 g L^{-1} + HCl 1.0 mL L^{-1}) and a $PdCl_2$ aqueous solution ($PdCl_2$ 0.1 g L^{-1} + HCl 1.0 mL L^{-1}) with washing by pure water between the immersions. During this procedure, the palladium ions were partly reduced into metallic fine particles by the reaction with stannous ions; $Pd^{2+} + Sn^{2+} \longrightarrow Pd^0 + Sn^{4+}$. The deposited utrafine palladium particles might work as catalysts for the electroless plating, and consequently, a thin palladium film was formed in the region where the surface was modified with the deposition of the utrafine palladium particles. Just before the electroless-plating, the support was immersed into a hydrazine aqueous solution. Note that the hydrazine was used as a reducing agent in the palladium electroless plating bath, and moreover, its concentration in the
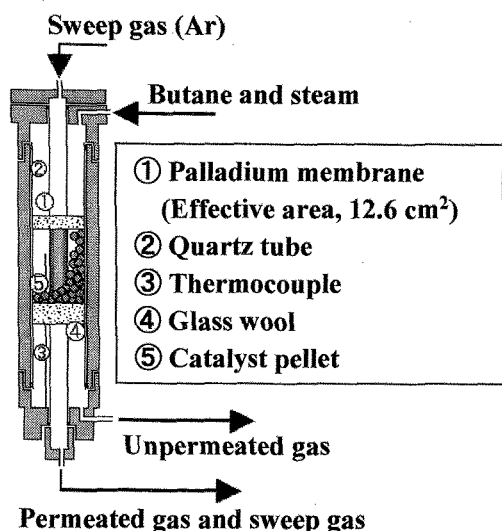
Fig. 1 Double tubular type membrane reactor

pretreatment solution (0.35 mL L^{-1}) was the same as in the bath. The thickness of the palladium film was controlled by the electroless plating time. The existence of pinholes and cracks were checked by a helium leakage test with a pressure difference of 2.0 kgf cm^{-2}. The details of the bath composition and conditions of the palladium electroless plating, and the characterization of the fabricated membranes were described in previous papers [7, 8].

### 2.2 Steam reforming of butane in membrane reformer

A double tubular type membrane reactor, as shown in Fig. 1, was used in this study. The inner tube was the supported palladium membrane fabricated in the above mentioned manner, while the outer tube was a quartz glass with an inner diameter of about 18 mm. Supported ruthenium reforming catalyst pellets with two types of metal loadings (0.5 and 2.0 wt.%), supplied from the N.E. CHEMCAT Corporation, were packed in the center region with a length of 40 mm between the tubes. Except for this region, the relatively thick layer of silver, through which hydrogen hardly permeates, was formed on the palladium film by an electroless-plating technique. Before the reactions, the catalyst and the palladium membrane were activated in a stream of hydrogen at 773 K. The mixture of butane and steam was quantitatively supplied to the reaction side of the reactor under the reaction conditions at a temperature of 773 K, a catalyst weight/butane flow rate (W/F) ratio of 10000 g-cat min C_4-mol^{-1}, and a steam/carbon (S/C) ratio of 3 mol mol^{-1}. Argon at a flow rate of 1 L min^{-1} was concurrently fed to the permeation side of the reactor in order to sweep the permeated hydrogen. The produced gas was analyzed by TCD- and FID-GC and its flow rate was measured by a soap film-type flow meter.

3. RESULTS AND DISCUSSION

3.1 Membrane Fabrication

It was reported in a previous paper that a dense palladium film having a thickness in the range of 4.5-20
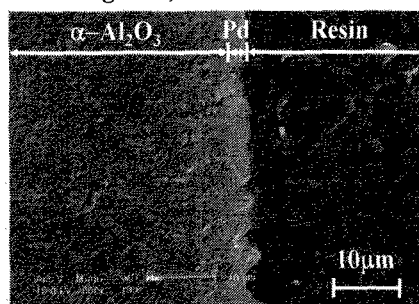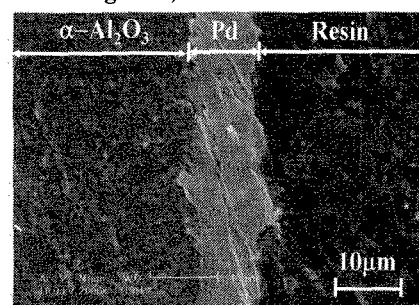

Fig. 2 Cross section view of supported palladium membranes prepared for different plating periods

µm could be fabricated on the outer surface of a commercially available porous inorganic tube by a 5-20 h electroless plating technique. Here, only a 1-h electroless plating formed a dense palladium film, where helium leakage was hardly observed. The improved characteristics are as follows:

1. The temperature of the surface activation procedure was increased from room temperature to 308 K.
2. The repeated number of the surface activation procedures decreased from ten to three.
3. The immersion of the support into a hydrazine aqueous solution was added just before the electroless plating.
4. The support was sufficiently warmed until the electroless plating temperature.
5. Bath load, defined as the ratio of the surface area of the support to the volume of the plating bath, decreased.

Figure 2 shows a cross section view of the supported palladium membranes that were prepared for different plating periods of 1 or 3 h. The corresponding averaged thicknesses of the palladium films were 3.9 and 10.2 µm, respectively. The thickness was proportional to the plating time. Incidentally, the surface morphologies, not indicated here, are almost the same as the ones prepared in the previously reported manner [7].
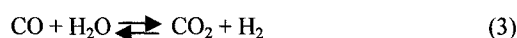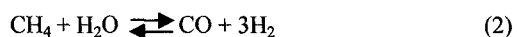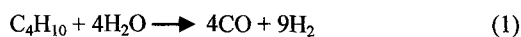
The hydrogen permeation coefficient measured by the permeation tests using pure hydrogen, i.e., hydrogen permeance standardized by membrane area, thickness, pressure difference, and time, also overlapped the data introduced in Steward's review article on the hydrogen permeability of various metals [9]. These results led us

to conclude that the mechanism of hydrogen permeation through the palladium film was not changed by the improvement; however, only the plating rate was accelerated.

The effect of the improvement of the palladium electroless plating including the surface activation procedure has not yet been completely clarified; however, we speculate that the immersion of the support into the hydrazine aqueous solution significantly affected the plating rate among the improved points. It is known that stannous chloride is easily oxidized in the atmosphere; therefore, a considerable amount of palladium ions were not reduced by the stannous ions, and still existed on the surface of the support using the previous procedure. The immersion into the hydrazine aqueous solution could reduce the unreacted palladium ions into the metal form. The increased plating rate is probably due to the increased density of the active palladium ultrafine particles working as catalysts for the electroless plating. However, it was observed by X-ray photoelectron spectrometry after the immersion into the hydrazine aqueous solution and the cleaning using distilled water that the stannous ions still coexisted with the palladium ultrafine particles. According to the report of Paglieri et al. [10], the amount of tin existing between the interface of a palladium film and a porous inorganic support was related to the stability of a supported palladium membrane at high temperature. Further study is required to remove stannous ions from the surface of a support.

3.2 Steam reforming of butane in membrane reformer

The steam reforming of butane is expressed as the following three reactions:

$$C_4H_{10} + 4H_2O \longrightarrow 4CO + 9H_2 \qquad (1)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (2)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (3)$$

Butane reacts with steam in the presence of an appropriate reforming catalyst such as a nickel or ruthenium-based catalyst, and then the produced gas becomes the corresponding thermodynamic equilibrium composition that is promptly determined by the reaction temperature, pressure, steam/carbon ratio (S/C), etc. If hydrogen is removed from the reaction field, the hydrogen yield can become independent of thermodynamic equilibrium limit in the closed system applicable to a conventional reactor.

Figures 3 and 4 indicate the carbon-based product composition and hydrogen yield in the steam reforming of butane in the membrane reformer incorporating with the supported palladium membrane prepared in the above manner. In Figure 4, the hydrogen yields with the thermodynamic equilibrium values are plotted as a function of the hydrogen separation ratio. Here, two supported palladium membranes having a different dense palladium film thickness (3.9 or 10.2 μm) were used in order to investigate the effect of hydrogen permeance on the reaction, and it was experimentally confirmed that hydrogen permeated through the membranes.

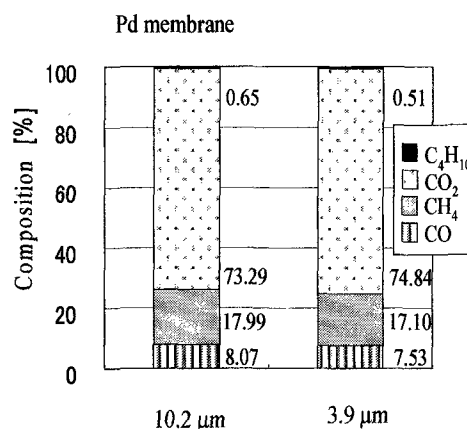It is found from Figure 3 that the methane and carbon

Pd membrane

Fig. 3 Carbon-based product composition in palladium membrane reactor having different thickness of palladium thickness
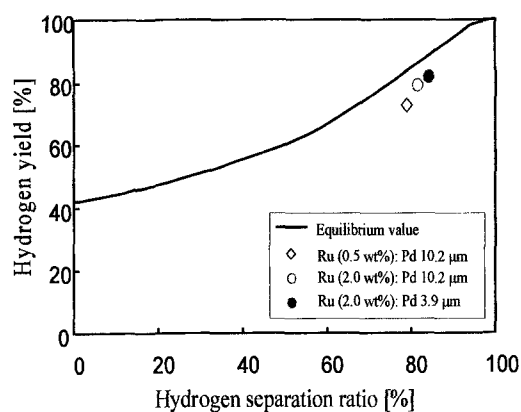

Fig. 4 Hydrogen yield as a function of hydrogen separation ratio with thermodynamic equilibrium values

monoxide concentrations had slightly decreased with the decreasing thickness of the palladium film. However, the decreasing degree was not as great as expected. The hydrogen permeance of the palladium membranes was inversely proportional to the thickness in the pressurized permeation experiments with pure hydrogen [2]. On the other hand, the permeance was hardly affected by the thickness for the atmospheric experiments using argon for sweeping the permeated hydrogen: 0.29 mol m^{-2} s^{-1} for a film thickness of 3.9 μm, and 0.23 mol m^{-2} s^{-1} for a film thickness of 10.2 μm. The slight decrease in the methane and carbon monoxide was due to the negligible effect of the thickness probably caused by the large resistance of the counter-diffusion of hydrogen and sweep argon in the pores of the support. In fact, the hydrogen yield was also slightly increased with the decreased thickness, as shown in Figure 4.

The effect of the ruthenium loading on the hydrogen yield is also shown. The hydrogen yield was found to be affected by the loading. The reforming temperature

was 773 K, which is relatively low compared with the temperature used in commercial reforming plants. The development of an active reforming catalyst working at a relatively low reaction temperature as well as a hydrogen separation membrane with an excellent hydrogen permeance and permselectivity should be required.

By the way, only a slight decrease in the hydrogen yield was observed in a series of experiments using a supported ruthenium catalyst and supported palladium membrane. Based on this result, it was postulated that the fuel for the steam reforming did not include a considerable amount of sulfur compounds, which were reported to be the cause of carbon deposition on the ruthenium catalyst [11].

CONCLUSIONS

An improved electroless plating procedure that includes the immersion of a support into a hydrazine aqueous solution just before dipping in the plating bath enables the fabrication of a supported palladium membrane having a high hydrogen permeance and permselectivity with a shorter plating time; namely, a film thickness of 3.9 μm was fabricated by only a 1-h plating. The resulting membranes having the different thicknesses of a palladium film was used for the steam reforming of butane, and the hydrogen yield did not increase even using a thinner supported palladium membrane, contrary to expectation. This result was due to the problem of mass transfer in the pores of the support.

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