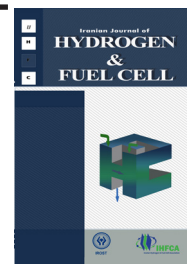Iranian Journal of Hydrogen & Fuel Cell

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Preparation of a Pd composite membrane via an organic-inorganic activation method in the electroless plating technique

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Article Information

Abstract

A palladium composite membrane was prepared via an electroless plating technique using the organic-inorganic method during the activation process. The ceramic support surface was modified by two TiO_2-boehmite and one γ-alumina layers to avoid Pd penetration in the support pores. A thin and defect-free Pd composite membrane was obtained by creating a relative smoothness on the ceramic support and using Pd nanoparticles in the activated layer. The resulting membrane showed an infinite selectivity for H_2/Ar with an H_2 flux in the range of 0.005-0.035 mol/m_2s depending on operating conditions. The hydrogen flux was linearly proportional to the pressure difference across the membrane at different temperatures and the pressure exponent n was very close to 1. According to the linear relationship of Arrhenius plot, the activation energy E_a of the Pd membrane was calculated to be 22.54 kJ/mol. H_2 permeance was kept over 0.023 mol/m^2s and the separation factor of H_2/Ar was over infinite at 773 K for 240 h, confirming a high potential of the prepared membrane in H_2 purification at high temperatures.

1. Introduction

Increasing demands for pure hydrogen in operation areas of fuel cells, petrochemical process, etc. make hydrogen production and purification very important [1-3]. Common hydrogen separation technologies involve solvent adsorption, pressure swing adsorption, cryogenic recovery and membrane separation. Among these methods, membrane separation technology has an economic potential to reduce operating costs, minimize unit operations and lower energy consumption [4]. The development of effective hydrogen membranes, such as the palladium membrane (due to high hydrogen permeance and selectivity versus other gases), has attracted considerable interest in industry requirements for commercial applications. Therefore, a lot of work has been done for the preparation and application of Pd membranes [5-8].

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Among the different methods to deposit thin Pd-based membranes on porous substrates, the electroless plating technique [9-12] provides strong advantages over other alternatives [13-15] such as the applicability to cost performance, non-conductive substrates with complex shapes and simple equipment. Electroless plating (ELP) includes the reduction of metal complex ions in a solution with the aid of a reducing agent without the application of an external electric field. For this method, an activation step is needed to initiate the reaction because the plated metal on the surface acts as a catalyst for further reaction [4]. Conventional electroless plating involves seeding a support surface with Pd precursor particles by sensitization, activation and plating of a Pd layer on the activated surface. Recently, other activation methods such as modified sol-gel [11], organic-inorganic method [7, 16], etc. have also been investigated, and each of them has advantages with respect to the conventional method [4]. For example, when using the organic-inorganic method the membrane stability was greatly improved by the forming of a small gap between the Pd-based membrane and porous substrate. Indeed, as reported in the literature [16, 17], the small space may make the whole Pd membrane move during stable thermal cycles because force is put on the whole Pd layer rather than on the small Pd anchor in the pores. Therefore, to prepare thin dense Pd-based composite membranes; the combined organic and inorganic method is a technique that shows high potential to obtain high hydrogen permeability and stability.

In order to lower the expense of Pd-based membranes, in most studies thin layers of Pd or Pd alloy are prepared on porous substrates. Ithas been concluded that the most desirable Pd membranes for practical applications should be prepared by the ELP method on porous alumina substrates [4]. However, these investigation results showed that the big pore size and roughness of substrate surfaces prohibited direct deposition of thin, defect-free Pd-based layers on the substrates. Introducing a micro and/ or mesoporous intermediate layer between the top Pd-based membrane and the porous substrate has been extensively applied to reduce the effect of the large

pore size and roughness of the substrates [11, 18].
In this work, for the first time two types of support modifications were applied to obtain relative smoothing of the ceramic support to avoid pinholes during the Pd composite membrane preparation process. After activation of the modified support by the organic-inorganic method, thin dense Pd composite membranes were fabricated by vacuum electroless plating (VELP) on the modified support. Hydrogen permeation performance through this Pd membrane was investigated. Finally, the long-term thermal durability was evaluated for a period of 240 h.

2. Experimental

2.1 Membrane fabrication

The homemade tubular alumina supports (average pore size 570 nm, porosity 38%, 10 mm outer diameter and 75 mm length) were made from high-quality α-Al_2O_3 powder (Fibrona Co.) via the gel-casting method [19]. Two types of intermediate layers were applied. The first type of intermediate layer was a TiO_2-Boehmite layer as reported in our previous work [20]. This layer was coated two times. The TiO_2-bohemite modified support was dipped into the aluminum alkoide sol for 10–30 s and then it was dried in air at room temperature for 12 h and calcined at 873K for 3 h [21]. This procedure was applied once.

For activation of the modified support, a polymer solution containing nanoparticles of Pd in a PEG matrix was used [22]. The activation procedure was repeated three times. Following the surface activation step, pre-electroless plating was done using a plating solution involving palladium chloride (2 g/L, Merck Co.) and EDTA sodium (Merck Co.) as a stabilizer. After that, the organic layer was removed at high temperature (873–973 K) in air atmosphere and reduced at 773-823 K for 3 h to activate the thin Pd layer for formal electroless plating.

A dense Pd layer would be deposited by the conventional vacuum electroless plating. The plating solution included $PdCl_2$ (3.6g/l, Merck Co.), Ethylene

diamine tetra acetic acid (Na$_2$EDTA, 76g/l, Merck Co.), ammonia (650ml/l, Merck Co.) and hydrazine (10ml/l, Acros Organics Co.). The whole bath system was placed in a thermostat chamber maintained at 333K by vacuum maintained inside the tubular support with a vacuum pump. The obtained palladium composite membranes were cleaned with ammonia solution and hot deionized water in sequence and then dried at 393 K.

2.2. Characterization techniques

An atomic force microscope (AFM, Thermo Microscopes) was used to study the surface roughness of the modified support. Also, to study surface morphology of the as-deposited palladium membranes and also to estimate the thickness of the Pd membrane, the scanning electron microscopy (SEM, Cam Scan MV2300 Czech Republic) was used. The distribution of palladium nanoparticles in the activated support was analyzed by EDX-SEM. The crystallite structure of activated support and composite membrane were characterized by X-ray diffraction (XRD, Siemens D500).

The gas permeation tests were measured on a homemade permeation apparatus as shown in Fig. 1. The side edge of the membrane was sealed by commercially graphite gaskets which can resist high temperatures. The permeated gas flow rate was measured with a soap bubble flow meter.

For high temperature testing, the prepared Pd membrane was heated under Ar atmosphere from room temperature to 673 K; the Ar gas was switched to pure H$_2$ for hydrogen activation treatment of the Pd membrane up to 723 K. After the hydrogen activation was completed and hydrogen permeance was constant, gas permeation tests were conducted with single gases (pure H$_2$ or Ar) or H$_2$–Ar binary mixtures over different pressures from 100 kPa to 500 kPa and at two different temperatures of 723 and 773 K. A bubble flow meter and an online gas chromatograph (Teif Gostar, Ind. Co.) were used for the permeated hydrogen to determine the flow rate and component of permeated gases, respectively. Finally, the membrane stability was evaluated by the hydrogen permeation flux versus the operation time at 773 K with a pressure difference of 200 kPa.

3. Results and discussions

3.1 The modified support
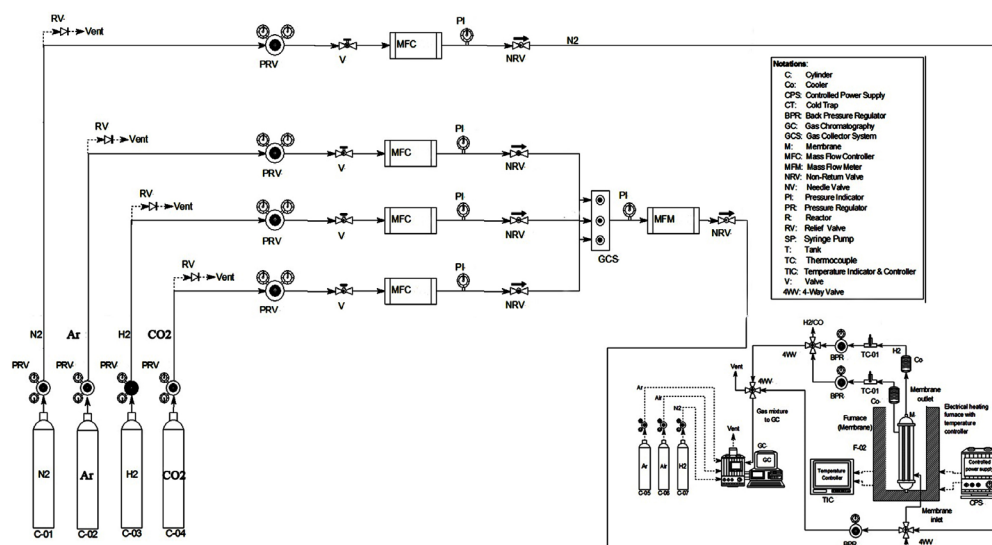
Introducing an intermediate layer between the top

Fig. 1. Schematic diagram of gas permeation apparatus.

Pd-based membrane and the porous support reduced any inherent defects of the support and prevented the infiltration of top layer material into the pores of the support. The AFM's capability to reconstruct the three-dimensional image of the modified surface can be exploited to obtain quantitative information about the surface roughness. Fig. 2 shows AFM images of the modified support surface. Nanoscope II software was used to perform a quantitative analysis of the surface roughness. As confirmed by the obtained results, the roughness of support was reduced on a nanometric scale after support modification.

3.2 Palladium membranes

Fig. 3 shows the EDX analysis of the surface of the activated support after coating with the Pd containing polymer template, confirming the attendance of Pd nanoparticles in the activated support. The particle size distribution of the synthesized Pd nanoparticles is presented in the inset of Fig. 3.

The peaks of the XRD pattern (Fig. 4) are assigned to the crystalline cubic form of metallic palladium in the activated support. It is obvious that the activated

support involves a large amount of palladium nanoparticles which has a strong effect on the quality of the electroless plated layer.
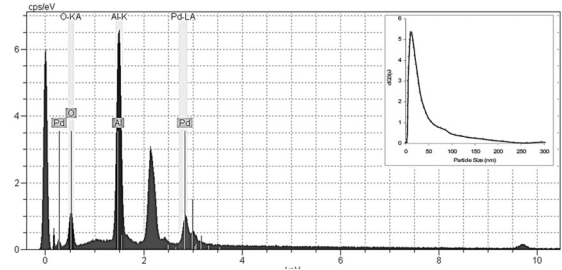

Fig. 3. SEM-EDX images of activated support.

The peaks of the XRD pattern (Fig. 4) are assigned to the crystalline cubic form of metallic palladium in the activated support. It is obvious that the activated support involves a large amount of palladium nanoparticles which has a strong effect on the quality of the electroless plated layer.

The XRD and SEM-EDS images of the as-prepared Pd composite membrane are also presented in Fig. 5. Fig. 5a shows the cross-section image of the Pd membrane which indicates a thin Pd layer (5 µm) deposited tightly on the surface of the porous support. Also,
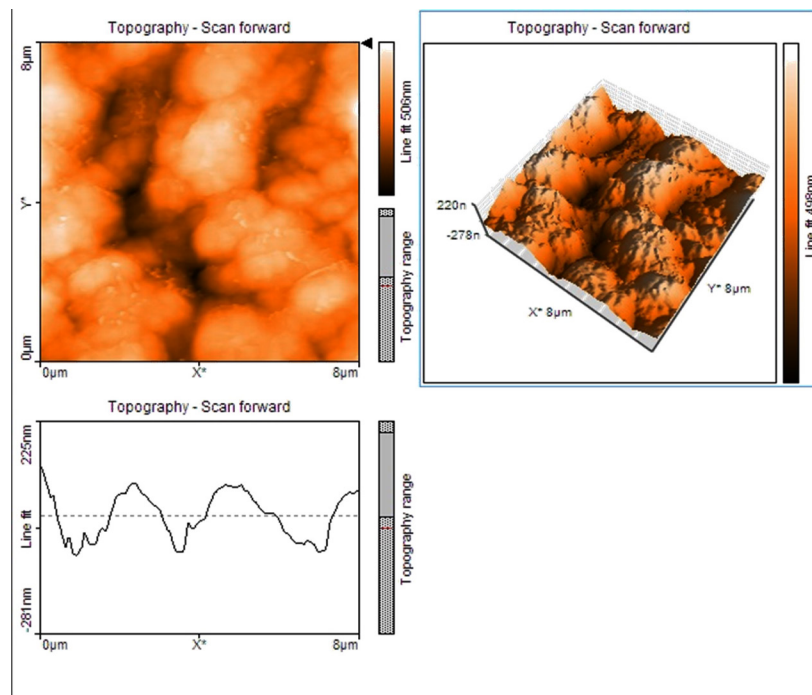

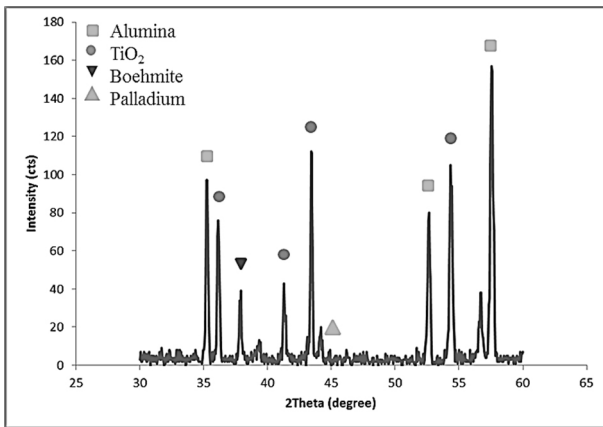**Fig. 2. AFM images of modified support.**

Fig. 4. XRD pattern of activated support.

the prepared Pd membrane has a finer and more uniform microstructure which is tightly packed together to form a dense Pd layer with many pinholes as illustrated in Fig. 5b. The peaks of the XRD pattern (Fig. 5c.) are assigned to the crystalline cubic form of metallic palladium.

3.3 The gas permeation of palladium composite membrane

Before the gas permeation tests at high temperatures, Ar permeation tests up to 200 kPa were done at room temperature to determine possible pinholes in the dense Pd layers. If no bubbles arise in the permeate side at 773 K, the membrane seemed suitable for high temperature testing.

Performance of the prepared defect-free Pd membrane was evaluated by single and binary gas mixtures of H_2 and Ar permeation tests. The Ar single gas and H_2–Ar binary mixtures permeation test confirmed no Ar permeation as determined by a GC analyzer at 723 K and 773 K at different pressures. So, the pure hydrogen flux versus pressure difference at different temperatures was investigated.

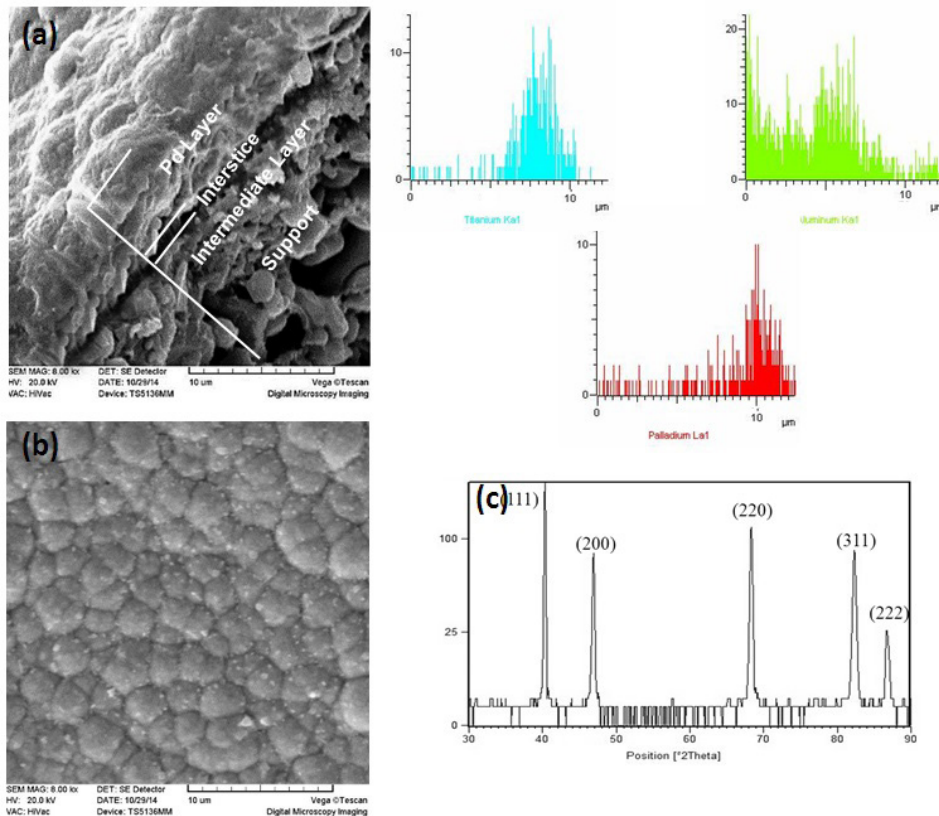Generally, the rate of hydrogen permeation can be expressed as follows:

Fig. 5. (a) SEM-EDS micrograph of the cross-section, (a) SEM micrograph of the surfaces-section and (c) XRD pattern of as-prepared Pd composite membranes.

$$J = Q\left(P_R^n - P_P^n\right) \qquad (1)$$

Where J is the hydrogen permeation flux, Q the hydrogen permeance, P_R and P_P the hydrogen partial pressure in the retentate and permeate, respectively, and n the pressure dependence factor (0.5–1). The factor n is equal to 0.5 when bulk diffusion through the dense P_d layer is the rate-controlling step, while the surface process of hydrogen dissociation adsorption and associative desorption is the rate determining step, n becomes equal to 1. An exponent of unity (n=1) suggests that permeation through the palladium is very fast and usually indicates that the palladium layer is thin, less than 5μm [7].

As shown in Fig. 6, hydrogen flux is linearly proportional to the pressure difference across the membrane at the investigated temperatures and the pressure exponent n is very close to 1. The obtained results confirmed the formation of a thin Pd composite membrane by the modified electroless plating method as developed in this research.
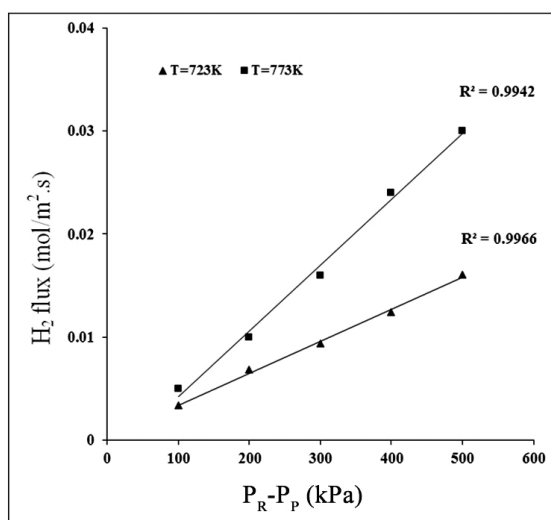

Fig. 6. Hydrogen flux versus operating pressure difference at different temperatures.

The correlation between temperature and hydrogen permeance can be expressed by an Arrhenius-type relation as follows:

$$Q = Q_0 \exp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

where Q_0 is a pre-exponential factor, E_a the activation energy, R the universal gas constant and T the absolute temperature. Fig. 7 demonstrates hydrogen permeation results obtained in this study in the form of an Arrhenius plot. According to the linear relationship of the Arrhenius plot, the activation energy E_a of the Pd membrane was calculated to be 22.54 kJ/mol. The value of the activation energy for the hydrogen permeation was similar to that reported in the literature [11].
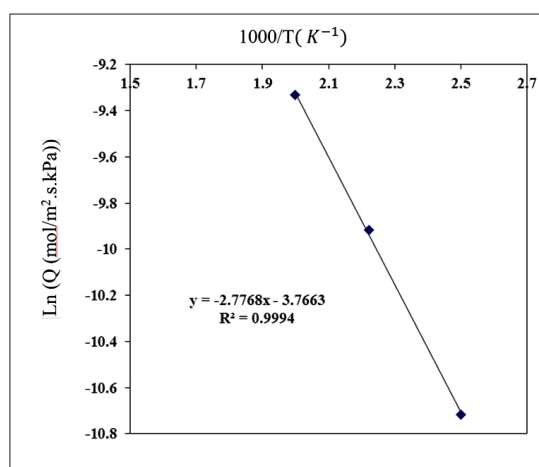

Fig. 7. The Arrhenius relation of hydrogen permeance with temperatures.

Finally, the hydrogen flux at a 773 K and pressure difference of 200 kPa versus the operating time was measured and the results are shown in Fig. 8. No significant changes in hydrogen flux were observed within the long operating time of 240 h. The gas exchange cycle between hydrogen and another inert gas (Ar) was used during operation time to check the stability of the membrane. The measurement of the Ar leak during the long-time operation progressively proved that the hydrogen separation factor was still infinite under experimental conditions. Therefore, the obtained results indicate that the prepared Pd membrane has very good stability.

The performance of Pd composite membranes reported in the previous literature and this work are summarized in Table 1. From Table 1, it can be seen that the Pd membranes prepared in this work exhibited higher permselectivity as well as other Pd composite
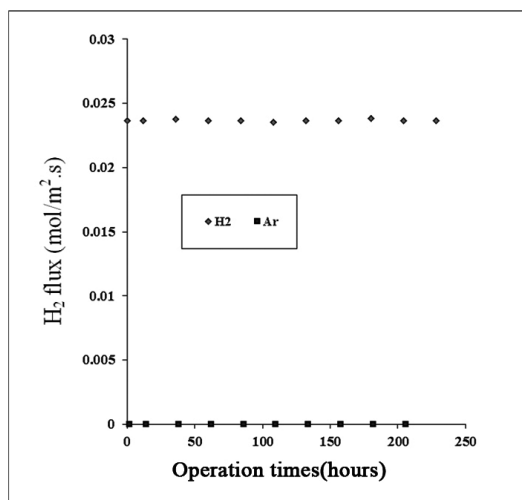
Fig. 8. Hydrogen flux versus operating time with gas exchanging cycles at 773 K with a pressure difference of 200 kPa.

high hydrogen permeance of 0.035 molm^{-2} s^{-1} and permselectivity of infinite at 773 K with a pressure difference of 500 kPa. Moreover, this membrane experienced the thermal durability tests over 240h under H_2 or Ar atmosphere for gas-exchanging cycles.

Acknowledgements

Table 1: Comparison of performance for Pd composite membranes in the literature and in this work

Membrane	Method	T(μm)	Selectivity	n	E_a (kJ/mol)	Ref.
Pd/SiO$_2$/PSS	ELP	5	H$_2$/N$_2$=300-450	1	24	[15]
Pd/Al$_2$O$_3$	ELP	5	H$_2$/He=∞	0.5	21.3	[7]
Pd/Al$_2$O$_3$	ELP	5	H$_2$/He=∞	0.5	17.78	[16]
Pd/Al$_2$O$_3$	ELP	5	H$_2$/Ar=0	1	22.54	This Work

membranes prepared by the ELP technique. Although the thickness of these Pd membranes is similar, the values of n and E_a were different. This is because the hydrogen permeance through Pd composite membranes is dependent not only on the thickness, but also on the fabrication methods and grain microstructure of the Pd membranes.

4. Conclusion

A new intermediate layer for relative smoothing of ceramic supports were proposed to plate a thin and defect-free Pd-based layer on the modified nanostructure support by the ELP method. By employing the organic-inorganic method during the activation process, Pd composite membranes with finer and more uniform microstructure were obtained. The membrane exhibited a high permeation performance and good thermal durability. The membrane showed a

5. References

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