INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–9

Available online at www.sciencedirect.com

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Hydrogen permeation in composite Pd-membranes prepared by conventional electroless plating and electroless pore-plating alternatives over ceramic and metallic supports

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ARTICLE INFO

Article history:
Received 6 March 2016
Received in revised form
25 May 2016
Accepted 14 June 2016
Available online xxx

Keywords:
Pd membrane
Alumina support
PSS support
Permeation behavior
Electroless plating
Electroless pore-plating

ABSTRACT

Composite palladium membranes are attracting great attention for hydrogen separation and membrane reactor applications, due to the complete hydrogen selectivity with reasonably high permeability and suitable mechanical stability. These membranes are usually prepared by depositing a thin Pd layer over ceramic or metallic supports, which give to the system the necessary mechanical resistance. The Pd incorporation is generally made by electroless plating (ELP), although there is still no fully optimized and universally accepted method, and many researches are currently devoted to the generation of thin and homogeneous metallic coatings with good adhesion and resistance to real conditions. Among the many studies, very few compares directly the properties of the two different supports (metallic or ceramic) on the overall membrane structure and performance. In the present work, the permeation behavior of several Pd-composite membranes, prepared by conventional ELP and by a novel pore-plating method (ELP-PP) has been studied on both ceramic and metallic supports. The membrane prepared over a tubular ceramic support by conventional ELP shows a permeability in the range of $2.5–3.6 \cdot 10^{-6}$ mol s^{-1} $bar^{-0.5}$ m, with nearly complete ideal selectivity and Pd thickness around 14 μm. With the alternative preparation method, ELP-PP, despite the lower Pd thickness, 8 μm, and also complete selectivity, lower hydrogen fluxes were observed with a permeability ranging from 5.8 to $8.5 \cdot 10^{-7}$ mol s^{-1} $bar^{-0.5}$ m. This behavior can be explained by considering that the pore-plating method leads to a Pd deposition over the external surface of the support but also inside the pores, generating an effective Pd thickness higher than that obtained with the conventional ELP. In this manner, the real behavior of the membrane is equivalent to a conventional 33 μm thick palladium layer. Finally, these results are compared replacing the ceramic support by a metallic one (PSS), which led to an increase in the minimum thickness necessary to achieve a totally dense membrane (Pd thickness, 9 μm), and, consequently, to a reduction of the observed transmembrane flux. However, in this case a lower deposition of palladium inside the pores of the support is observed thus causing a lower resistance to the hydrogen permeation with respect to ceramic supported membranes.

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http://dx.doi.org/10.1016/j.ijhydene.2016.06.128

Introduction

Hydrogen is considered one of the best alternatives for development of future environmental friendly power generation devices, although it needs to be produced from diverse raw materials [1]. Amongst these, methane or bio-alcohols reforming and biomass gasification are currently the main technologies for starting up a feasible hydrogen economy [2]. In all these cases, hydrogen is generated with other subproducts, although its use in fuel cell systems requires very high-purity in order to avoid poisoning with carbon monoxide or other residual products. For this reason, forecasts indicate a significant increase of ultra-pure hydrogen demand for next decades [3] and result in the need of development of additional separation and purification steps for low-cost hydrogen production [4].

Membrane technology, especially when Pd-based membranes are considered, can be a good solution for H_2 purification and pre-combustion CO_2 sequestration both in downstream independent separators and in a membrane reactor, combined with a catalyst [1]. Pd-based membranes can be prepared over different porous supports by a wide variety of techniques, such as cold-rolling [5], physical or chemical vapor depositions [6,7], electrodeposition [8] or electroless plating [9]. However, the latter is one of the most interesting due to the achievable good coverage and the experimental simplicity [9,10]. This alternative consists of immersing the support in an aqueous solution of the metal, typically in a complex form with ammonia and EDTA, and adding a reducing agent in order to incorporate the pure palladium over the external surface of the support. Based on this technique, a new alternative method, the so-called Electroless Pore-Plating (ELP-PP) technique, has been recently developed to prepare completely dense membranes minimizing the generation of defects. It consists on forcing the reaction between Pd source and reducing agent to take place inside the pores by feeding reactants from opposite sides of the support [11]. Usually, both techniques, conventional ELP and ELP-PP, are applied to inorganic supports in order to minimize the noble metal thickness, maintaining good H_2 selectivity and suitable mechanical resistance [11,12]. A wide variety of materials have been proposed as support for the preparation of these composite membranes, including Vycor glass [13], metals [14,15] or ceramics [16,17]. The selection of an appropriate material as support is crucial, although the perfect solution is not found. Metallic supports, indeed, are endowed with a good compatibility with the Pd layer and an exceptional mechanical resistance that makes the integration in current facilities, usually made in stainless steel, easier. However, this type of supports also has a very rough surface with large pores distribution, which makes difficult the generation of an ultra-thin and continuous Pd layer [18]. On the other hand, ceramic supports present a very smooth surface with a narrow pore size distribution that could overcome this problem [19,20]. Unfortunately, these supports present a lower mechanical resistance than metallic ones and the thermal expansion coefficient, significantly different from that of palladium, could also represent an inconvenience for an adequate lifespan of the composite membranes [19]. In spite of the lack of an ideal solution, to the best of our knowledge, it is really difficult to find a rigorous comparison of diverse types of supports in the preparation of composite membranes for hydrogen separation. In general, authors select a particular type of support, usually metallic or ceramic, analyzing the palladium incorporation by diverse techniques or methods and characterizing the composite membranes in terms of morphology and permeability. In some cases, it is possible to find some modifications of the support in order to improve the thin hydrogen selective layer [21–26], but the direct comparison of totally different supports is really scarce in the open literature.

Trying to address this problem, the present work shows a double comparison for the preparation of a composite Pd membrane: i) First, conventional electroless plating (ELP) and electroless pore-plating (ELP-PP) techniques have been applied over a ceramic support in order to compare the metallic film properties achieved by both alternatives. ii) After that, the influence of the support has been also analyzed for the membrane preparation via ELP-PP, comparing the presented results with the previously published ones [27–29], where a metallic support was used.

Materials and methods

A set of membranes were prepared varying both support type (metallic and ceramic) and Pd incorporation method (ELP and ELP-PP). Metallic supports, provided by Mott Metallurgical, are made of porous stainless steel with a media grade of 0.1 μm, outside diameter 1.29 cm and active length of 7.00 cm, as previously published [27–29]. The ceramic ones are formed by asymmetric layers of α-Al_2O_3-γ-Al_2O_3, produced by Inopor GmbH, with an outside diameter of about 1.00 cm and an active length of 10.00 cm. The main difference between both types of supports, in addition to the material composition, is the surface properties. In this manner, the metallic supports present a relative rough surface with really wide pore sizes (up to 30 μm), while the ceramic ones were characterized by a narrow surface pore size distribution in the order to 70 nm. In both cases, the extremes of the membranes were treated for sealing purpose by adding fully dense stainless steel tubes or endowing them with a glazed end in case of metallic or ceramic supports, respectively.

The incorporation of the selective Pd layer has been achieved by two different techniques: i) conventional electroless plating (ELP) and electroless pore-plating (ELP-PP). The general procedure for palladium coating over the external surface of the supports consists of three successive steps: i) initial cleaning, ii) activation and iii) palladium deposition. More details about the experimental procedure, reactants and particular conditions can be found elsewhere [27–29]. The main difference between both techniques is how the reactants are put in contact, as shown in a simplified scheme in Fig. 1. As it can be seen, the palladium source (Pd-ammonium complex) and the reducing agent (hydrazine-based solution) are fed in a different way for each case. When conventional ELP technique is used, both reactants are fed from the external side of the support. On the other hand, when ELP-PP is used,

Please cite this article in press as: Alique D, et al., Hydrogen permeation in composite Pd-membranes prepared by conventional electroless plating and electroless pore-plating alternatives over ceramic and metallic supports, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.06.128