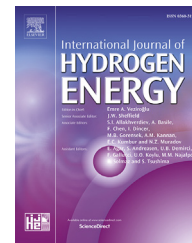




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Graphite coating on alumina substrate for the fabrication of hydrogen selective membranes

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ABSTRACT

Development of composite membranes is a suitable alternative to improve the hydrogen flux through palladium membranes. The porous substrate should not represent a barrier to gas permeation, but the roughness of its surface should be sufficiently smooth for the deposition of a thin and defect-free metal layer. In this study, the performances of the modification of the outer surface of an asymmetric alumina hollow fibre substrate by the deposition of a graphite layer were evaluated. The roughness of the substrate outer surface was reduced from 120 to 37 nm after graphite coating. After graphite coating, the hydrogen permeance through the composite membrane produced with 2 Pd plating cycles was of $1.02 \times 10^{-3} \text{ mol s}^{-1} \text{ m}^{-2} \text{ kPa}^{-1}$ at 450 °C and with infinite H_2/N_2 selectivity. Similar hydrogen permeance was obtained with the composite membrane without graphite coating, also at infinite H_2/N_2 selectivity, but 3 Pd plating cycles were necessary. Thus, graphite coating on asymmetric alumina hollow fibres is a suitable alternative to reduce the required palladium amount to produce hydrogen selective membranes.

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Introduction

Hydrogen is a high value chemical commodity besides being considered as the energy vector of the future. The main route for hydrogen production is the steam reforming of fossil fuels [1]. After reaction, hydrogen should be separated from other gas products to the required purity that could be up to 99.99%. Pressure swing adsorption (PSA) process is conventionally applied for hydrogen separation, but this process presents some limitations such as large cost of the PSA unit, difficulty to use it on smaller portable scales and poor recovery levels of hydrogen from feed gases [1,2]. Palladium (Pd) membranes offer a suitable alternative to separate hydrogen from a gas

mixture at infinite selectivity [1]. However, the main drawbacks for application of Pd membranes in hydrogen purification are related to hydrogen-induced embrittlement phenomenon (phase change when operated below the critical point), surface poisoning by contaminants (carbon monoxide, carbon dioxide, steam, sulfur species, and others), high palladium cost (at nearly \$30/g, \$800/oz [3]) and low hydrogen permeance in Pd membranes of high thicknesses [4,5]. To overcome the two first drawbacks above, Pd has been suggested to be alloyed with a series of other metallic elements such as Ag, Cu, Ni, Pt and Au [6]. Related to the two last drawbacks, the enhancement of hydrogen permeation and the reduction of membrane cost may be achieved by the

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deposition of a thin and defect-free Pd layer on a porous substrate. While Pd foil membranes need a thickness of at least 25 μm in order to have a minimum mechanical stability, the thickness of the palladium layer can be reduced to less than 5 μm in supported membranes without losing the membrane selectivity [7]. Different supports are reported in the literature, including Vycor glass, ceramics and stainless steel [8], which presents different costs, mechanical and thermal resistances and gas permeances.

Moreover, the pore size of the substrate surface is certainly a challenging on depositing a thin and pinhole free palladium film. Ma et al. [9] suggested the thickness of the deposited palladium layer should be at least three times greater than the substrate surface pore size. The deposition of an intermediate layer between the substrate and the palladium membrane is a suitable alternative to decrease the support roughness and the pore size of its external part in order to improve the deposition of a thin and defect-free selective palladium layer. Wei et al. [10] modified the surface of a porous stainless steel (PSS) by scraping it with a calcined 2B pencil lead. Nayebossadri et al. [11] showed that the deposition of tungsten powder decreased the surface pore size of a PSS substrate besides acting as an effective inter-diffusion barrier. In fact, the use of PSS supports requires a pre-treatment to improve the substrate surface and to prevent intermetallic diffusion between Pd and PSS at high temperatures [12].

Alumina is a ceramic material widely applied to produce Pd composite membranes due to its availability and mechanical and thermal stabilities. Alumina substrates can be configured in different geometries including flat discs, tubes and hollow fibres. Hollow fibre geometry presents the main advantage of reducing the filtration module area in addition to the simplicity of sealing a bundle of fibres outside of the hot zone of the separator [13]. Furthermore, the support can be specifically fabricated with the asymmetric pore structure in which long filaments and a sponge-like layer are formed across the fibre and on its outer surface, respectively [14]. Applying the phase inversion method, regions of different pore sizes are formed in the support without requiring a multi-step process that is onerous due to the constraint of the sintering process at high temperature in each step [15]. Palladium can be deposited on the sponge-like layer of the fibre that presents relative low pore size. However, some penetration of Pd into the outer surface of asymmetric ceramic supports was previously reported [16] so that the decrease of the surface pore size and roughness may be recommended. Guo et al. [17] proposed the deposition of a layer containing silicalite-1 zeolite on macroporous alumina support prior to the palladium electroless plating. Tong et al. [18] coated a polymer precursor layer of poly(2,6-dimethyl-1,4-phenylene oxide) onto a alumina hollow fibre substrate in order to decrease the interstitial penetration of palladium through the porous support. Guo et al. [19] coated the outer surface of a porous alumina tube with a PVA film and improved the H_2/N_2 selectivity of the deposited Pd membrane from 58 to 956. Hu et al. [20] diminished the rough of the outer surface of a macroporous alumina tube by scratching it with a 2B pencil, but the achieved H_2/N_2 selectivity of the 5 μm palladium membrane was of 3700 at 1 bar and 723 K.

In this study, the development of a high permeable and selective composite alumina/graphite/palladium membrane

for hydrogen purification is proposed. Asymmetric alumina hollow fibres were fabricated with the desired morphology to be used as the membrane substrate. A thin graphite layer was deposited on the outer surface of the hollow fibre to act as an effective palladium barrier. This low cost intermediate layer will prevent palladium penetration through the substrate and, thus, less palladium will be required to have a selective membrane. Different thicknesses of palladium layers were deposited on the substrate in order to obtain a membrane with high hydrogen selectivity.

Experimental

Materials

Aluminum oxide powders with particle size lower than 1 μm (alpha-phase, 99.9% (metal basis), surface area 6–8 $\text{m}^2 \text{g}^{-1}$) were purchased from Alfa Aesar and were used as supplied. Polyethersulfone (PESf, Verdal 3000P, Solvay), dimethyl sulfide (DMSO, Vetec, Brazil) and Arlcel P135 (Croda, Brazil) were used as binder, solvent and additive, respectively. Tap water was used as external coagulant. Tetraamminepalladium(II) chloride monohydrate (99.99% metals basis, Sigma-Aldrich), Ethylenediamine tetraacetic acid (EDTA, Sigma-Aldrich), ammonium hydroxide (28%, Vetec, Brazil) and hydrazine hydrate (Sigma-Aldrich) were used for preparing the plating solution, and tin(II) chloride dehydrate (puriss. p.a., Sigma-Aldrich), hydrochloric acid (37%, Vetec, Brazil) and palladium (II) chloride (99.999%, Sigma-Aldrich) were used for preparing the activation/sensitizing solutions.

Fabrication of the asymmetric hollow fibre

The asymmetric alumina hollow fibre was produced by the phase inversion technique followed by a sintering step according to the parameters suggested by Gil et al. [16], Terra et al. [21]. The suspension solution was prepared by dissolving the additive (Arlcel) in the solvent (DMSO) followed by the addition of the required amount of alumina powder. The solution was agitated for 48 h in a ball mill. Subsequently, the polymer (PESf) was added and the mixture was agitated for further 48 h. The prepared suspension solution had a concentration of 0.4 wt % of Arlcel, 36.1 wt% of DMSO, 58.0 wt% of alumina and 5.5 wt % of PESf. Prior to extrusion, the ceramic suspension was degassed using a vacuum pump at 850 mmHg for 2 h and, then, it was transferred to a 200 mL stainless syringe. The suspension was extruded through a tube-in-orifice spinned (OD 3 mm, ID 1.2 mm), without air gap and pure DMSO was used as bore fluid. The flows of ceramic suspension and internal coagulant were controlled and monitored at 15 mL min^{-1} using two individual pumps (Harvard Apparatus, model XHF). The hollow fibre precursors were left 48 h into the coagulant bath to complete phase inversion, and then washed with water and sintered in a furnace (Carbolite TZF 15) following 3 temperature ramps: 1) from room temperature to 300 $^\circ\text{C}$ at the rate of 1 $^\circ\text{C min}^{-1}$, 2) from 300 to 600 $^\circ\text{C}$ at the rate of 2 $^\circ\text{C min}^{-1}$ with a dwelling of 60 min, and 3) from 600 to 1350 $^\circ\text{C}$ at the rate of 5 $^\circ\text{C min}^{-1}$ with a dwelling of 5 h. The temperature was then reduced to room temperature at the rate of 5 $^\circ\text{C min}^{-1}$. The target temperature

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