Metallic nickel hollow fiber membranes for hydrogen separation at high temperatures

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ABSTRACT

Metallic nickel dense hollow fiber membranes were fabricated by a combined spinning and high-temperature sintering technique. Hydrogen permeation through the nickel hollow fiber membranes was measured at high temperatures up to 1000 °C using H_2-containing gas mixtures fed on the shell side and N_2 as the sweep gas in the fiber lumen. The experimental results indicated the sintering should be carried out at around 1400 °C for 3 h, under a hydrogen-containing atmosphere so as to reach the required densification of the nickel hollow fiber membranes. Hydrogen permeation through the dense nickel hollow fiber membranes is controlled by H-atom diffusion through the membrane bulk, and can be well described by the Sieverts' equation with the activation energy of 51.07 kJ mol^{-1}. For the hollow fiber with wall thickness of 256 μm, the hydrogen permeation flux value reached up to 7.66×10^{-3} mol m^{-2} s^{-1} at 1000 °C with 100% H_2-permselectivity. The Ni hollow membrane exhibits high stability in CO_2, CO or steam containing atmospheres, and demonstrates a potential use in hydrogen production by high temperature hydrocarbon reforming reactions.

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1. Introduction

Hydrogen is not only an important raw material for chemical and petrochemical industries, but also a potential clean fuel to mitigate the global climate change caused by the excessive greenhouse gas emissions. Pure hydrogen does not exist as a natural resource like coal, oil and methane and it has to be produced from hydrogen-containing compounds, where a safe, low-cost and highly efficient separation and purification technology for hydrogen production is always required. The membrane technology based on Pd and its alloy membranes represents a promising method, since the palladium composite membranes can not only be applied for manufacturing hydrogen separators, as a consequence of their high permeability and selectivity towards hydrogen [1–3], but also can be directly integrated into membrane reactors for producing ultra-pure hydrogen via reforming of hydrocarbons and alcohols with high yields [4,5]. However, the palladium membranes have the unavoidable shortcomings such as high material cost, thermal instability and embrittlement due to the phase transition (phase α to hybrid phase β) at low temperatures in the presence of hydrogen [6,7].

The high and variable cost of palladium evokes the development of less expensive alternatives to the Pd-based membranes. The transition metals with a body-centered cubic structure such as V, Ta and Nb exhibit very high hydrogen permeability, but are also prone to embrittlement failure, due to excessive hydrogen adsorption [1]. By alloying with Ni and/or Ti to reduce the hydrogen absorption to levels where mechanical stability is greatly improved, the embrittlement tendency for these metal membranes can be reduced [8–10]. Such alloy membranes for hydrogen separation demonstrate a significant performance/cost saving over Pd-based alloys [11]. However, these transition metals exhibit a high reactivity with gases to form dense oxide/nitride layers over their surfaces, leading to considerable reduction in the hydrogen permeation through the resultant membranes. Moreover, Pd-alloy catalyst layers at both membrane surfaces (typically 500 nm or less) are still required in order to promote dissociation of hydrogen and to prevent inhibition by CO, H_2S and steam gases.

Nickel is another promising alternative for the applicability of hydrogen separation membranes with much reduced price [12–15]. Like metal palladium, nickel also can absorb hydrogen, although the solubility in nickel is lower than in palladium. The solid-phase diffusion in a defect-free Ni film is inefficient

compared to that in a dense palladium hydride [14,15]. As a consequence, the Ni membranes generally exhibit a much lower hydrogen permeability than the Pd-based membranes, since the permeability can be approximated as the product of absorption and diffusivity. To obtain a high hydrogen permeation flux, the nickel membrane has to be reduced in thickness. Ernst et al. [14] prepared a nickel film of 1–1.5 μm in thickness on an asymmetric tubular alumina support by electroless plating technique using hydrazine as the reducing agent. The microstructure and permselectivity of the membrane were stable up to 600 °C. Although the hydrogen permeability of the Ni/ceramic composite membrane was close to the values given for the Pd-based membrane in the literature, the hydrogen permselectivity was much lower, indicating the deposited Ni membrane was not dense. Better hydrogen selectivity can be obtained with Ni–P or Ni–B amorphous alloy/ceramic membranes, which are prepared by using sodium hypophosphite or sodium borohydride as the reducing agent [16,17], but these membranes show limited thermal stability and a deteriorating performance at high temperatures. Moreover, the hydrogen permselectivity is also just above the Knudsen value, suggesting the presence of pores through the nickel film.

The objective of this work was to fabricate metallic nickel dense hollow fiber membranes for pure hydrogen separation. The hollow fiber configuration allows for a very high surface-area-to-volume ratio (up to $\sim 10^4\,\mathrm{m}^{-1}$) and a small effective membrane thickness, which can provide a much lower permeation resistance than the conventional thicker planar or tubular membranes [18–23]. Therefore, a high hydrogen production rate can be expected in the case of a hollow fiber membrane module with a large specific membrane area, even though the permeability of the individual membrane is low. A combined phase inversion and sintering technique was applied for the preparation of dense Ni hollow fiber membranes [24]. The preparation conditions and the hydrogen permeation behavior through the Ni hollow fiber membranes have been extensively investigated. To our knowledge, this is the first report of hydrogen permeation behavior through the Ni hollow fiber membranes.

2. Experimental

2.1. Preparation of the nickel hollow fiber membranes

Nickel hollow fiber membranes were fabricated through the combined phase inversion and sintering technique [19,25]. Polysulphone (PSf, Udel® P-3500, Solvay) was dissolved in N-methyl-2-pyrrolidone (NMP: Electronic grade, Shandong Qingyun Changxin Chemical Science-Tech Co. Ltd., China) to form a polymer solution. Nickel powder with the average particle size of 1–1.5 μm and 99.9% purity supplied by Shenzhen Gem High-Tech Co. Ltd. (China) was added to the polymer solution, followed by stirring for 36 h to ensure uniform dispersion of the nickel particles. The resultant spinning solution was composed of 66.67 wt% Ni powder, 6.67 wt% PSf, and 26.66 wt% NMP. After degassing, the spinning solution was transferred to a stainless steel container and then pressurized with nitrogen through a spinneret with the orifice/needle tube diameter of 3.0/1.5 mm into a tap water tank, with deionized water as the core liquid, to form hollow-fiber precursors. The hollow fiber precursor was immersed in water for 24 h to fully consolidate the porous structure. In order to obtain pure nickel dense hollow fiber membranes, a well-designed sintering program was performed. Prior to sintering, the hollow fiber precursor was dried and straightened. Then, the fiber precursor was placed inside the tubular furnace, heated at 3 °C/min to 600 °C and calcined in static air for 1 h to burn out the organics. Subsequently, a 50 mol% H₂–N₂ mixture in 30 mL/min flow rate was

Table 1
Preparation conditions of the metallic nickel hollow fibers.

Experimental parameters		Values
Compositions of the starting solution	Ni powder (1–1.5 μm)	66.67, wt%
	PSf, Udel® P-3500	6.67, wt%
	NMP	26.66, wt%
Spinning temperature		25 °C
Injection rate of internal coagulant		0.14 cm³ s⁻¹
Nitrogen pressure (absolute pressure)		0.15 MPa
Air gap		0.5 cm
Sintering atmosphere		50 mol% H₂–N₂
Sintering temperature		1200–1400 °C
Dwelling time		3 h

introduced into the furnace, and the temperature was then raised at a heating rate of 3 °C/min to above 1200 °C, dwelling for 3 h to obtain a dense membrane. After sintering, the membrane was cooled down to room temperature at 3 °C/min still under the H₂-containing protecting atmosphere. The operating conditions employed to prepare the nickel hollow fibers are summarized in Table 1.

2.2. Hydrogen permeation measurement

In order to measure the hydrogen permeation properties of the nickel hollow fiber membranes, a home-made permeation cell was assembled as schematically shown in Fig. 1. A gas-tight Ni hollow fiber of about 100 mm in length, which was tested to be completely gas-tight at room temperature in advance, was connected on both ends to two alumina tubes (Ø4 mm diameter and 160 mm length) by a high temperature sealant. It was then housed in a quartz tube (Ø10 mm diameter and 400 mm length) covered by two caps on both ends to form a permeation cell. The permeation cell was placed inside a furnace having a 50 mm effective heating length. In operation, the H₂-containing gas mixture was fed in the shell side while the sweep gas nitrogen was flowing in the fiber lumen to collect the permeated hydrogen. In order to evaluate the effect of water vapor on the hydrogen permeation performance, the H₂-containing gas feed was passed through a water bath at 30 °C prior to flowing into the hollow fiber; in this case, the vapor concentration in the feed was 3.8 mol%. The gas flow rates were controlled using mass flow controllers (D07-7B, Beijing Sevenstar Electronics Co. Ltd., China), and were also measured with a soap bubble flow meter. Compositions of the permeate gas were detected online using a gas chromatograph (Agilent 6890N) fitted with a 5 Å molecular sieve column (3 mm diameter and 3 m length) and a TCD detector. Highly pure argon was used as the GC carrier gas and the flow rate was controlled at 20 mL min⁻¹. The hydrogen permeation flux and separation factor were calculated by

$$J_{H_2} = \frac{V_t}{A_m}\left(y_{H_2} - \frac{x_{H_2}}{1 - x_{H_2}}y_i\right) \tag{1}$$

$$\alpha_{H2-i} = \frac{y_{H_2}/y_i}{x_{H_2}/x_i} \quad (i = \mathrm{He},\ CO_2\ \mathrm{or}\ CO) \tag{2}$$

where V_t is the effluent flow rate of the permeate stream; x_{H_2} is the hydrogen concentration in the feed stream; y_{H_2} and y_i are the hydrogen and the diluting gas fractions in the permeate stream, respectively, and A_m is the effective membrane area for hydrogen permeation, which was calculated by $A_m = \frac{\pi(d_{out}-d_{in})L_e}{\ln(d_{out}/d_{in})}$ in which L_e is the effective fiber length for hydrogen permeation (50 mm) and d_{out}, d_{in} are the outer and inner diameter of the hollow fiber