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CO_2-tolerant U-shaped hollow fiber membranes for hydrogen separation

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ABSTRACT

Tungstates (Ln_6WO_{12}) are considered as one of the most promising candidates for hydrogen separation membrane materials. Among varies Ln_6WO_{12} materials, the molybdenum doped neodymium tungsten oxides have attracted increasing attention due to their sufficient mixed proton-electron conductivity and high tolerance towards acid gases, such as CO_2 and H_2S. The hydrogen permeation properties of the U-shaped $Nd_{5.5}W_{0.5}Mo_{0.5}O_{11.25-\delta}$ (NWM) hollow fiber membranes have been studied systematically in this work. A high hydrogen permeation flux of 1.29 mL/min·min^2 was obtained at 975 °C using 80% H_2–20% He as feed gas and humidified Ar as sweep gas. Furthermore, the U-shaped NWM hollow fiber membrane present a hydrogen permeation flux with only a slight decrease during 80 h's operation feeding with the CO_2-containing gas.

Introduction

Mixed proton-electron conducting (MPEC) ceramic materials have gained considerable attention in recent years, which can be used as hydrogen separating membranes and catalytic membrane reactors (CMRs) at elevated temperatures [1,2]. The MPEC membranes exhibit good H_2 selectivity and thermal stability with low cost and easy manipulation when applied in H_2 separation. Most studies on MPEC membranes are focused on the perovskite-type oxides, such as doped $BaCeO_3$, $SrCeO_3$ and their derivatives [3–14], which present relatively high hydrogen permeation fluxes [15–20]. However, the industrial applications of these MPEC membranes are always hampered by their poor chemical stability. Because H_2 is mainly produced from the reforming of fossil fuels followed by the water-gas shift reaction with CO_2-containing fuel gas [21]. The perovskite-type oxides, normally containing alkaline-earth metal ions, are known to be instable in CO_2-containing atmospheres due to the reaction between the alkaline-earth metal ions and CO_2 [22–25]. Therefore, the development of the MPEC membranes with good chemical stability against CO_2 is urgent for their applications in H_2 separation. Recently, tungstates (Ln_6WO_{12}), a new kind of MPEC ceramic materials, have attracted extensive attentions [26,27] because of their good stability to acid gases [28–30] and sufficient ambipolar conductivity [26,31–34]. Escolastico et al. [35] found that the $Nd_{5.5}WO_{11.25-\delta}$ compound exhibited excellent chemical stability in CO_2-rich and sulfur-containing atmospheres with a moderate hydrogen permeation flux. In order to further improve its hydrogen permeability, partial substitution of W with Mo was proved to be an effective approach. A hydrogen

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permeation flux of 0.30 mL/min·cm^2 through a disk-shaped $Nd_{5.5}W_{0.5}Mo_{0.5}O_{11.25-\delta}$ membrane was achieved [36], which was higher than that through many other tungstates-based membranes. This result implies that Mo-doped $Nd_{5.5}WO_{11.25-\delta}$ could be a promising candidate for hydrogen separation and purification.

However, the hydrogen permeation flux through the disk-shaped membrane is still not high enough, which is difficult to meet the requirement for practical application. An efficient way is to reduce the membrane thickness and the hollow fiber configuration would be one kind of proper alternative. In recent years, extensive efforts have been made in the preparation of hollow fiber membranes via a combined phase inversion and sintering technique. The hollow fiber membranes could provide more effective membrane area per volume with thinner thickness around 200 μm, which is beneficial for H_2 transportation. Hollow fiber membranes can be sealed easily at high temperatures compared with the disk-shaped membranes [37–42]. Furthermore, as a special geometry of hollow fiber, the U-shaped hollow fiber membranes can be sealed to the module facilely avoiding the mechanical break during heating and cooling process due to its free expansion or shrinkage at varying temperatures [39].

Herein, the MPEC material of $Nd_{5.5}W_{0.5}Mo_{0.5}O_{11.25-\delta}$ (NWM) compound is chosen and the U-shaped NWM hollow fiber membranes are prepared successfully by phase inversion spinning technology. Hydrogen permeation properties and its chemical stability under CO_2-containing atmosphere of the U-shaped NWM hollow fiber membranes have also been investigated.

Experimental

NWM powder was prepared using a conventional solid state reaction method. Stoichiometric amounts of Nd_2O_3 (99.9%), WO_3 (99.0%), MoO_3 (99.5%) were mixed by ball-milling for 10 h with acetone as dispersion medium. The resultant mixture was then dried, grinded and calcined at 900 °C for 10 h in order to form the good phase structures. For the following phase inversion process, the calcined powder was ball-milled again with acetone for 10 h followed by sieving through a sifter of 200-mesh to exclude the agglomerates.

The U-shaped NWM hollow fiber membranes were fabricated through a wet-spinning phase-inversion combined with sintering technique [28,36,39]. The spinning slurry was composed of 55.10 wt% NWM powder, 35.15 wt% N-methyl-2-pyrrolidone (NMP) as the solvent, 8.52 wt% poly-ethersulfone (PESf) as the polymer binder, and 1.23 wt% polyvinyl pyrrolidone (PVP) as the additive. Deionized water and tap water were used as the internal and external coagulants, respectively. The parameters of the wet-spinning procedure were presented in Table 1. After the wet-spinning phase-inversion, the green (in web version) precursors of the hollow fiber membranes were firstly immersed in the deionized water for 24 h to ensure the enough solidification. Then the hollow fiber membrane precursors were dried in air for more than 24 h at room temperature. And then they were sintered at 1500 °C in ambient static air for 10 h to remove the polymers and obtain the gastight membranes.

Table 1 – Parameters for the U-shaped NWM hollow fiber membranes preparation via phase inversion technology.

Parameter	Value
Composition of the starting solution	
NWM powder	55.10 wt%
PESf A-300	8.52 wt%
NMP	35.15 wt%
PVP, K30	1.23 wt%
Spinning temperature	25 °C
Air gap	1 cm
Spinning pressure	0.1 bar
Internal coagulant rate	2 mL/min

The phase structures of the as-prepared NWM powder and the hollow fiber membranes were characterized using X-ray diffraction (XRD, Bruker-D8 ADVANCE, and Cu Ka radiation). Thermogravimetric analysis (TG) was performed with a NETZSCH instrument (STA449C) at a heating and cooling rate of 10 °C/min under CO_2 or N_2 from room temperature to 800 °C. The microstructures of the U-shaped NWM hollow fiber membrane precursor and the as-sintered hollow fiber membrane were studied by a Scanning Electron Microscope (SEM, JEOL JSM-6700F).

The hydrogen permeation properties of the U-shape NWM hollow fiber membranes were investigated in a home-made

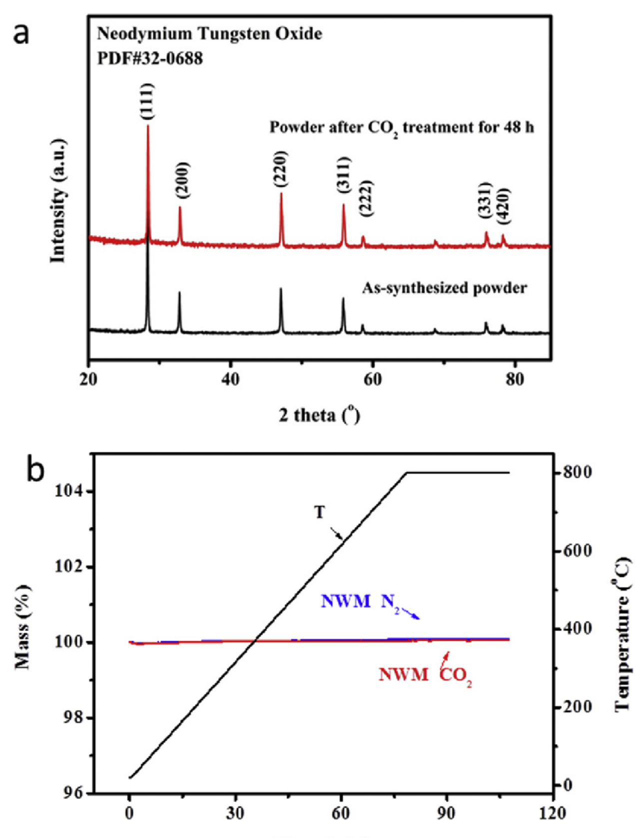

Fig. 1 – (a) XRD patterns of the NWM powders before and after CO_2 treatment at 900 °C for 48 h; (b) Thermogravimetric curves of the NWM powder under CO_2 and N_2 atmospheres.