



Metalloid phosphorus cation doping: An effective strategy to improve permeability and stability through the hydrogen permeable membranes

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ABSTRACT

Metalloid element doping is a novel strategy to improve the properties of hydrogen permeable membranes. Herein, phosphorus doping was applied to enhance the hydrogen separation performance of lanthanum tungstate membrane for the first time. The effects of P content on the hydrogen permeability of $\text{La}_{5.5}\text{W}_{0.6}\text{Mo}_{0.4-x}\text{P}_x\text{O}_{11.25-8}$ ($x = 0, 0.05, 0.1, 0.2$) membranes were firstly investigated under different temperatures. Among series of doped-membranes, $\text{La}_{5.5}\text{W}_{0.6}\text{Mo}_{0.35}\text{P}_{0.05}\text{O}_{11.25-8}$ exhibited increased hydrogen permeability and improved stability than the parent material due to higher protonic conductivity. The results showed that metalloid phosphorus element doping possesses a beneficial effect on the hydrogen separation performance, which could accelerate the development of the hydrogen permeable membranes and promote their practical applications.

1. Introduction

Hydrogen is considered as a promising clean energy because of its high heat value, which attracting lots attentions. In industrial scale, hydrogen is mainly produced from the steam reforming of methane (SMR), which needs further purification [1]. Nowadays, hydrogen can be separated by three major processes: pressure swing adsorption, cryogenic distillation and membrane separation [2–6]. Among them, membrane separation technology is considered as an energy-saving and recycling method, forwarding to reap great global benefits [7–9].

Recently, mixed protonic and electronic conductor (MPEC) oxides are attracting more attentions as they can separate hydrogen in protons form at specified conditions [4,10]. Thus, the hydrogen selectivity of MPEC membranes are infinite theoretically in the dry reducing atmosphere [4]. For industrial applications, both high hydrogen permeability and good stability of MPEC membranes are required. Until now, MPEC oxides applied in hydrogen separation membranes can be classified into perovskite oxides based on cerate (ACeO_3 , $A = \text{Ba}, \text{Sr}$, etc.) and fluorite-type oxides based on $\text{Ln}_6\text{WO}_{12}$, ($\text{Ln} = \text{La}, \text{Nd}, \text{Er}$, etc.) [11,12]. The perovskite oxides own high protonic conductivity when exposed to reducing atmosphere at high temperature, while their hydrogen permeation fluxes are too low to meet the industrial demands. In order to improve their hydrogen permeability, trivalent metal ions such as Tb [13], Yb [14–20], Y [21–23], Sm [24,25], Nd [26], Eu [25,27], Fe [28] were doped into Ce site, resulting in improved

hydrogen permeation performance.

Aside from the perovskite oxides, lanthanum oxides $\text{La}_6\text{WO}_{12}$ are recently been applied in hydrogen separation as their high protonic conductivity at high temperature [29–31]. The hydrogen permeation flux through $\text{La}_{5.6}\text{WO}_{11.25-8}$ membranes with 0.5 mm thickness reached $0.047 \text{ mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ at 1000°C [31]. To further improve the hydrogen permeability of $\text{La}_6\text{WO}_{12}$, partially introduction of Nd into La were studied, such as $(\text{La}_{5/6}\text{Nd}_{1/6})_{5.5}\text{WO}_{12-8}$, $\text{Nd}_{5/6}\text{Ln}_{1/6}\text{WO}_{12-8}$ ($\text{Ln}: \text{La}, \text{Ce}, \text{Pr}, \text{Eu}, \text{Tb}$) [32,33]. Besides, different metal cations substituted W^{6+} by Mo^{6+} [34–38], Nb^{5+} [39–41], Re^{4+} [42] were reported to enhance the hydrogen permeability. The substitution W^{6+} with 40 mol. % Mo^{4+} shows the reported highest hydrogen permeation flux of $1.36 \text{ mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ at 975°C through the U-shaped $\text{La}_{5.5}\text{W}_{0.6}\text{Mo}_{0.4}\text{O}_{11.25-8}$ hollow fiber at 975°C in humid hydrogen atmosphere [37,43]. Despite the metal cations doping, anion doping in oxygen sites in lanthanum oxides was another novel method to enhance the hydrogen permeation flux. In our previous work, it was reported that the fluoride metalloid anion-doped lanthanum tungstate membranes exhibited twice higher hydrogen permeability at 950°C than that of its parent one [44,45]. However, during the long-term test at 950°C , its hydrogen permeation fluxes decreased sharply due to the Mo^{6+} reduction [44].

Except metal cation and metalloid anion doping, metalloid cation doping might be another effective method to improve the conductivity and stabilize the phase structure of oxides. Slater and co-workers

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studied the effect on the incorporation of metalloid cation phosphorus (P) into perovskite oxide CaMnO_3 , finding the $\text{CaMn}_{0.95}\text{P}_{0.05}\text{O}_{3-\delta}$ owned higher conductivity than the undoped oxides [46]. Enhancement in conductivity was also observed when P doped into $\text{Ba}_{0.33}\text{Sr}_{0.67}\text{Co}_{0.76}\text{Fe}_{0.19}\text{P}_{0.05}\text{O}_{3-\delta}$ oxide at 700 °C [47]. Moreover, the P element could stabilize the brownmillerite crystal structure and enhanced its conductivity of $\text{Ba}_2\text{In}_2\text{O}_5$ oxide [48]. Through metalloid cation P doping, the $\text{SrCoO}_{3-\delta}$ oxide changed from hexagonal to stable tetragonal structure [49–51]. Therefore, the metalloid P doping might be an effective strategy to modify the materials properties, which was not applied in the development of MPEC membranes for hydrogen purification until now.

Herein, the metalloid P cation-doped $\text{La}_{5.5}\text{W}_{0.6}\text{Mo}_{0.4-x}\text{P}_x\text{O}_{11.25-\delta}$ ($x = 0, 0.05, 0.1, 0.2$ hereafter LWMP x in abbreviation) hydrogen permeable membranes have been synthesized for the first time. The influence of P on the conductivity, hydrogen permeability and stability of LWMP x membranes are investigated in detail.

2. Experimental section

LWMP x ($x = 0, 0.05, 0.1, 0.2$) powders were synthesized with La_2O_3 , WO_3 , MoO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ by traditional solid-state method. Firstly, La_2O_3 was pretreated at 1000 °C for 2 h in order to remove the absorbed water and carbon dioxide. Stoichiometric ratios of La_2O_3 (Sinopharm Chemical Reagent Co., Ltd, 4 N), WO_3 (Sinopharm Chemical Reagent Co., Ltd, 99%), MoO_3 (Kermel, 99.5%), $\text{NH}_4\text{H}_2\text{PO}_4$ (Aladdin, 99%) were mixed by ball-milling at a speed of 300 rpm for 10 h in acetone as a solvent. The resultant mixture were dried at room temperature for 36 h after the solvent evaporated. After being dried completely, the mixture were calcined at 1000 °C for 10 h in the oven. Finally, the obtained precursor were uniaxially pressed at 18 MPa for 10 min to gain the green disks. Then to get the gas-tight membranes for the following permeation tests, the green disks were sintered at 1500 °C for 10 h. Each gas-tight membrane was tested at the room temperature by pressure-holding test in order to confirm it was dense enough. Subsequently, the gas-tight membranes for hydrogen permeation test were polished by the SiC paper to get the uniform 0.5 mm thickness.

The crystal structures of membranes were measured using X-ray powder diffraction (XRD, Bruker-D8, Cu K α radiation). Total Pattern Solution (TOPAS) software was used to calculate the cell parameters and cell volume of membranes based on the Rietveld method. The surficial and cross-sectional morphology of the membranes were observed by scanning electron microscopy (SEM, Hitachi SU 8220) at electron voltage of 10 kV. Energy dispersive X-ray spectroscopy (EDXS, Horiba, X-MaxN detector) was used to determine the elements component of membranes.

The X-ray photoelectron spectroscopy (XPS) analysis data were recorded on Thermo Scientific EscaLab 250Xi spectrometer equipped with an Al-K α X-ray source. Transmission electron microscope combined with EDXS (TEM, FEI Tecnai G2 F30) was applied to test the elements distributions.

Before conductivity test, the membranes were polished to be square. Two parallel silver wires were twined on the membrane surface, followed by the silver slurry painted on. Then the disks were calcined at 600 °C for 2 h to make the organic matter of the slurry volatilized. During the conductivity test, membranes were measured at constant voltage 3 V (potentiostat, Fujian Chang Lian Electron Co., Ltd.) under humid 10 vol% H_2/He atmosphere, ranging from 600 °C to 850 °C with a ramp rate of 5 °C $\cdot\text{min}^{-1}$.

Temperature programmed reduction (TPR) tests of LWM and LWMP0.05 powders acquired from sintered membranes were measured by using automatic chemical adsorption instrument (Micromeritics, AutoChem II 2920). At first, the powders were pretreated by He for 30 min, then they were placed to the reduction condition under 10% H_2/Ar atmosphere from 50 °C to 800 °C with a heating rate of 10 °C $\cdot\text{min}^{-1}$.

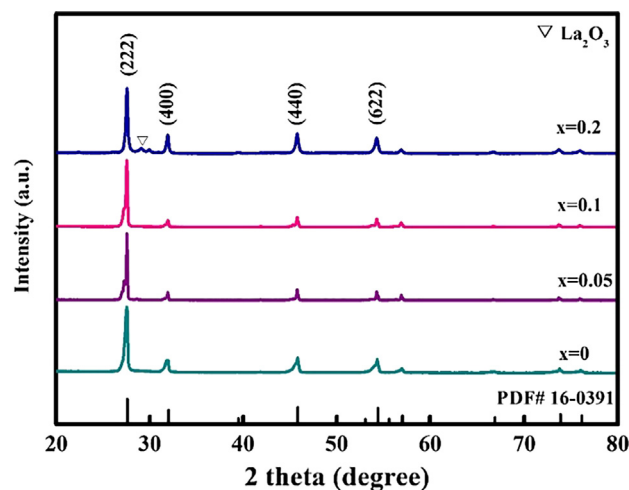


Fig. 1. XRD patterns of fresh LWMP x ($x = 0, 0.05, 0.1, 0.2$) membranes calcined in air at 1500 °C for 10 h.

Table 1

Crystal symmetry, cell parameters and cell volumes of the LWM, LWMP0.05, LWMP0.1 membranes modified from the TOPAS software. Values in parentheses are standard deviations.

Materials	Crystal symmetry (space group)	Cell parameter (nm)	Cell volume (nm ³)
LWM	Cubic <i>Fm</i> 3 <i>m</i>	1.1169(2)	1.3933(3)
LWMP0.05	Cubic <i>Fm</i> 3 <i>m</i>	1.1166(4)	1.3923(2)
LWMP0.1	Cubic <i>Fm</i> 3 <i>m</i>	1.1164(5)	1.3916(2)

Table 2

Valence state and effective ionic radius of elements containing in $\text{La}_{5.5}\text{W}_{0.6}\text{Mo}_{0.4-x}\text{P}_x\text{O}_{11.25-\delta}$ ($x = 0, 0.05, 0.1, 0.2$) oxides.

Elements	Valence state	Effective ionic radius (Å)	Electronegativity
La	+3	1.032	1.10
W	+6	0.60	2.36
Mo	+6	0.59	1.16
P	+5	0.38	2.19
O	-2	1.38	3.44

For hydrogen permeation test, the membranes were sealed by glass ring (Schott, 8253) at a home-made reactor described in our previous work [52–55]. The flow rate of H_2/He mixture gas as the feed side was 80 mL $\cdot\text{min}^{-1}$, while Ar is applied as the sweep gas. The flow rate and composition of the effluent was tested by using a soap bubble meter and a gas chromatography (GC, Agilent, 7890A) equipped with thermal conductivity detector respectively. The hydrogen permeation flux can be calculated from the equation as follows:

$$J_{\text{H}_2} (\text{mL} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}) = \left(c_{\text{H}_2} - c_{\text{He}} \times \frac{\sqrt{2} F_{\text{H}_2}^{\text{feed}}}{F_{\text{He}}^{\text{feed}}} \right) \times \frac{F}{S}$$

where c_{H_2} and c_{He} are the H_2 and He concentrations on the sweep side, that can be read from the GC instrument. $F_{\text{H}_2}^{\text{feed}}$ and $F_{\text{He}}^{\text{feed}}$ are the flow rates of the H_2 and He on the feed side, which can be adjusted by the mass flow controller (Yudian Automation Technology Co., Ltd.). F denotes the flow rate of the sweep side effluent sent to the GC, and S denotes the membrane effective permeate area. During all the hydrogen permeation test, the percentage of the leakage of H_2 due to the

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