Enhancement of oxygen permeation through U-shaped K$_2$NiF$_4$-type oxide hollow fiber membranes by surface modifications

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The U-shaped ($\text{Pr}_{0.9}\text{La}_{0.1})_{2}$(Ni$_{0.74}$Cu$_{0.21}$Ga$_{0.05}$)O$_{4+\delta}$ (PLNCG) hollow fiber membranes are prepared by a phase inversion spinning process. The membranes are modified by acid etching followed by a porous catalytic layer coating of La$_2$Sn$_2$CoO$_{6.2}$ (LSC) aiming to improve the surface exchange kinetics, thus increasing the oxygen permeation flux. The oxygen permeation fluxes through the unmodified/acid etched/acid etched followed by LSC coated PLNCG hollow fiber membranes are measured under air/He gradients. At 800 °C, the oxygen permeation flux through the unmodified membrane is 0.06 ml/min cm$^2$, while it rises to 0.21 ml/min cm$^2$ after surface modification. The surface modified hollow fiber membrane exhibits noticeably higher oxygen permeation flux than that through the unmodified membrane, especially at relatively low temperatures, which indicates the membrane surface modification is beneficial for improving the oxygen permeation.

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1. Introduction

In recent decades, the mixed conducting ceramic oxides with oxygen ionic and electronic conductivity (MIEC) have gained increasing attention due to their potential applications in the oxygen separation [1,2], conversion of natural gas [3–7] the cathode of solid oxide fuel cell [8,9] and oxygen supplying to power stations with CO$_2$ sequestration according to the oxy-fuel concept [10–12]. There are two basic requirements for the MIEC membranes in industrial applications. Firstly, the MIEC membranes should have a good stability under various atmospheres at elevated temperatures for a fairly long time, especially under some harsh reducing atmosphere, such as CO, H$_2$, CH$_4$ and CO$_2$. Secondly, the MIEC membranes should exhibit remarkable high oxygen permeation fluxes. In recent years, many efforts have been focused on improvement of the oxygen permeation of these MIEC membranes. Under an oxygen partial pressure gradient at elevated temperature, oxygen permeation through the MIEC membrane takes place by five major steps: (i) the oxygen molecule in air diffusing from the gas phase to the membrane surface; (ii) oxygen exchange reactions on the high oxygen partial pressure side of the membrane surface, including oxygen adsorption, dissociation and incorporation to form lattice oxygen; (iii) bulk diffusion of oxygen ions or vacancies and electron holes; (iv) surface reaction between lattice oxygen and electron holes on the other membrane surface (permeate side) and oxygen desorption; (v) recombination of the oxygen molecule which leaves the membrane surface to the permeate stream. It is clear that the major resistance of oxygen permeation results from surface reactions and bulk diffusion. If the rate controlling step of the oxygen transporting is only the bulk diffusion, the oxygen permeation flux can be increased by reducing the membrane thickness. Various coating technologies can be used for preparation of the super thin dense MIEC membrane supported on porous substrate [13,14]. Hollow fiber membrane with wall thickness between 200 and 300 μm is also a good choice to decrease the bulk diffusion resistance and improve the oxygen permeation flux [15–19]. As is known, when the membrane becomes sufficiently thin, the surface reaction begins to control the rate of oxygen permeation [20]. Under this circumstance, further increase of the oxygen permeation rate can be achieved by improving the surface exchange kinetics. It be realized (i) by increasing the effective membrane surface area, such as coating the membrane surface with porous layer [21,22], roughening the membrane surface by abrading [23,24], acid-modification [25] and methane-modification [26]; (ii) by coating the membrane surface with materials of superior oxygen exchange properties as catalyst to promote a faster oxygen exchange, such as the noble metals [27–33].

In our previous work (Pr$_{0.9}$La$_{0.1}$)$_2$(Ni$_{0.74}$Cu$_{0.21}$Ga$_{0.05}$)O$_{4+\delta}$ (PLNCG) is proved to be a good K$_2$NiF$_4$-type oxide for oxygen permeation with an excellent chemical stability in the long-term operation, especially under CO$_2$ atmosphere, which promotes the practical application in oxy-fuel combustion for CO$_2$ capture of MIEC membranes [34,35]. However, the oxygen permeability through PLNCG hollow fiber membrane should be further...
improved. The oxygen permeation process through the hollow fiber membranes may be largely controlled by the surface exchange reactions at the gas/membrane interfaces [31,32]. Therefore, enhanced oxygen permeation fluxes through the hollow fiber membranes can be expected by surface modifications. Herein, La$_{0.8}$Sr$_{0.2}$CoO$_3$ (LSC) was chosen as the catalytic material to modify the PLNCG hollow fiber membrane surface due to its good catalytic activity and good stability under air [36]. In this paper, the PLNCG hollow fiber membranes are modified by acid etching followed by LSC porous layer aimed to increase the oxygen permeation flux. The surface modified hollow fiber membrane is used for the oxyfuel combustion, etc., only the inner surface of the hollow fiber membrane is exposed to the harsh atmosphere, while the outer surface of the membrane is still exposed to air. Considering the good stability of LSC under air and good stability of PLNCG under even harsh conditions, herein, only the outer surface of the hollow fiber membrane was coated with LSC. The effects of the membrane outer surface modification on the oxygen permeation flux have been investigated.

2. Experimental

2.1. Preparation of powder

The sol–gel route based on citric acid and EDTA as complexing and gelation agents has been adapted to prepare the PLNCG and LSC powder [34]. Taking PLNCG as an example, Ga was dissolved in nitric acid first, and proper amounts of Pr(NO$_3$)$_3$·6H$_2$O, La(NO$_3$)$_3$·6H$_2$O, Ni(CH$_3$COO)$_2$·4H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O were dissolved in water followed by the addition of citric acid, EDTA and NH$_3$·H$_2$O. The mixture was then evaporated at 150°C under constant stirring to obtain a dark-green gel. The gel was firstly ignited to flame. After combustion, precursor-powder can be achieved, which does not present desired phase structure. Therefore, the precursor-powder was ground and calcined at temperatures up to 950°C for 10 h with a heating rate of 2°C/min to remove the residual carbon and form the desired K$_2$NiF$_4$-type structure. For spinning hollow fiber membranes, the powder was ball-milled for 24 h and then was dried using a spray dryer (Büchi Mini Spray Dryer, B-290) with a nozzle of 1 μm.

2.2. Preparation of hollow fiber membrane

The U-shaped PLNCG hollow fibers were fabricated using a wet spinning/sintering technology [37]. The spinning solution was composed of 9.29 wt.% polyethersulfone (PESf, A-300, BASF), 37.18 wt.% 1-methyl-2-pyrrolidinone (NMP, AR Grade, purity > 99.8%, Kermel Chem Inc., Tianjin, China), 0.93 wt.% polyvinyl pyrrolidone (PVP, K30, Boao biotech co., Shanghai, China) and 52.60 wt.% PLNCG powder. A spinneret with an orifice diameter and inner diameter of 1.5 and 1.0 mm, respectively, was used to obtain the hollow fiber precursors. Deionized water and tap water were used as the internal and external coagulants, respectively. Afterward, the PLNCG hollow fiber precursors were sintered at 1300°C for 3 h with the air flow rate of 60 ml/min to remove the polymer and get gas-tight membrane.

Membrane surface modification was carried out by two steps, which is shown in Fig. 1. Firstly, the U-shaped PLNCG hollow fiber membrane (Fig. 1A) was modified by acid etching aimed to get a large effective membrane surface area (Fig. 1B). In briefly, the U-shaped hollow fiber membrane was immersed in 18 vol.% HCl solution for 5 min with slow stir. The etched hollow fiber was rinsed with deionized water for three times and dried at room temperature. Secondly, the coating slurry was prepared by mixing of LSC and ethanol in an agate mortar. The LSC slurry was brushed onto the outer surface of the acid-modified U-shaped PLNCG hollow fiber membrane, as shown in Fig. 1C. The coating slurry was prepared by mixing of LSC and ethanol in an agate mortar. The LSC slurry was brushed onto the outer surface of the acid-modified U-shaped PLNCG hollow fiber membrane, as shown in Fig. 1C. The surface coating process was repeated for twice after the coating layer dried at room temperature. There is no annealing process after the acid-treatment or coating the catalysis layer. Finally, the U-shaped PLNCG hollow fiber membrane after surface acid-modification and LSC porous layer-modification (Fig. 1D) was prepared for oxygen permeation.

2.3. Characterizations and measurements of oxygen permeation

The phase structure of the as-prepared PLNCG powder, LSC powder and the modified hollow fibers were characterized by X-ray diffraction (XRD, Bruker-D8 ADVANCE, Cu Kα radiation). The microstructure and morphology of the surface modified PLNCG hollow fiber membranes were observed by a scanning electron microscope (SEM, JEOL JSM-6490LA). The element compositions

Fig. 1. Schematic diagram of the surface modification of PLNCG hollow fiber membrane.
of the membranes were determined by energy dispersive spectros-
copy (EDS). The oxygen permeation fluxes through the modified 
and unmodified U-shaped PLNCG hollow fiber membranes 
were investigated in a high-temperature permeation cell [38]. Before 
the modified hollow fiber membrane is used for the oxygen perme-
ation, the gas tightness is tested at room temperature. No nitrogen 
is detected on the shell side even when the nitrogen partial pres-
sure on the core side reached 0.5 MPa, which indicates that the 
hollow fiber membranes are gastight. The U-shaped PLNCG hollow 
fiber membrane was sealed in a corundum tube with two channels 
by a commercial ceramic sealant (HT767, Hutian, China). Air or a 
mixture of nitrogen and oxygen was fed to the shell side while he-
lium swept on the core side to collect the permeated oxygen 
through the membrane. The gas flow rates were controlled by mass 
flow controllers (MFC, Seven Star D08-4F/ZM) calibrated using a 
soap bubble flow meter. The composition of the permeated gas 
was measured using an online gas chromatograph (GC, Agilent 
7890) with a TCD detector. The leakage of the oxygen due to the 
imperfect sealing at high temperatures was less than 0.5% during all 
the experiments. The calculation of oxygen permeation flux 
can be found in our previous work [37].

3. Results and discussion

Fig. 2 shows the XRD patterns of LSC powder, unmodified/acid 
etched/acid etched followed by LSC-coated PLNCG hollow fiber 
membranes. The XRD patterns show strong diffraction peaks as-
signed to the orthorhombic phase of LSC mainly with 2θ of 23.2, 
33.1, 40.6, 59.3, 69.4, 79.1 for the lattice planes of 110, 112, 022, 
220, 312, 224 and 116, respectively. The unmodified PLNCG hollow 
fiber membranes shows good K2NiF4-type structure mainly with 2θ 
of 24.1, 31.6, 32.8, 44.0, 47.1 and 57.8 for the lattice planes of 111, 
113, 200, 204, 220 and 313, respectively. Comparing with the XRD 
pattern of the unmodified membrane, it can be seen that some 
peaks assigned to CuCl have occurred on the XRD curve of the 
HCl-modified hollow fiber membrane. The membrane surface com-
position before and after acid-treatment have also been checked 
through EDS characterization, which shows that a small amount of 
Cl remains on the membrane surface after the acid etching. 
Wang et al. [25] found that acid etching didn’t lead to the forma-
tion of new phases, but only changed the microstructure on hollow 
fiber surface. It is because La0.6Sr0.4Co0.2Fe0.8O3 

acid etched followed by LSC-coated PLNCG hollow fiber membranes.
becomes less important as the temperature further decreases. It can be found the enhancement factor of acid etching followed by LSC coating is 3.6 at 800 °C and it rises to 10.3 at 750 °C. The oxygen permeation flux through the modified membrane can even improved with the enhancement factor of 25.3 at 700 °C.

**Fig. 6** compares the oxygen permeation fluxes through the unmodified/acid etched/acid etched followed by LSC coated hollow fiber membranes as a function of helium sweep flow rates at 825 °C. Generally, the oxygen permeation fluxes through the membrane increased with increasing helium flow rate. Because higher helium flow rates dilute the permeated oxygen and lower the oxygen partial pressure on the core side, i.e. increase the permeation driving force. However, the effect of the helium flow rate on the oxygen permeation flux through PLNCG hollow fiber membrane becomes insensitive when the temperature is below 900 °C [38]. Even so, the improvement of the oxygen permeation flux after surface modification is still obvious. The enhancement factor of acid etching followed by LSC coating keeps around 2.3 at 825 °C, which is in accordance with the result in **Fig. 5**.

The oxygen permeation fluxes through the unmodified/acid etched/acid etched followed by LSC coated hollow fiber membranes as a function of oxygen partial pressure on the shell side
at different temperatures are shown in Fig. 7. The total flow rate of the oxygen and nitrogen on the shell side is 120 ml/min and different oxygen partial pressure on the shell side is obtained by adjusting the ratio of nitrogen and oxygen. Both of the oxygen permeation fluxes through the unmodified and modified membranes increase with increasing oxygen partial pressure on the shell side because of the increased oxygen gradient across the membrane. As is known, there are two ways to increase the oxygen gradient, increasing the feed air pressure by a compressor, or reducing the permeate pressure by using a vacuum pump. In fact the latter has a larger impact, as reducing the pressure of the permeate flux will result in higher oxygen fluxes for a given air feed pressure. From Fig. 7, the positive effect of the surface modification on the oxygen permeation flux is more remarkable at relatively low temperature, which is in accordance with the results in Figs. 4 and 5. Furthermore, the oxygen permeation flux through the modified membrane is more sensitive to the oxygen partial pressure on the shell side. It is because the driving force, the oxygen partial pressure gradient across the membrane, has a larger influence on the bulk diffusion than that on the surface oxygen exchange [38]. After the surface modification, the surface reaction resistance is reduced. However, the surface kinetic is still controlling the oxygen ionic transport, which is still the limiting transport condition even after surface modification.

Fig. 8 shows the apparent activation energy of these hollow fiber membranes. Three straight lines are found which give the apparent activation energy of 112.74, 94.13 and 44.80 kJ/mol for the unmodified, acid etched, acid etched followed by LSC coated PLNCG hollow fiber membranes, respectively, at the temperature range of 700–900 °C. As is known, the apparent activation energy of the oxygen permeation is consisted of two parts: (i) the activation energy of the surface oxygen exchange, and (ii) the activation energy of the bulk diffusion. After the surface modification, the resistance of the surface reaction is reduced. As a result, the apparent activation energy of the modified PLNCG hollow fiber membrane is decreased from 112.74 kJ/mol to 44.80 kJ/mol, which indicates the improvement of the oxygen permeability.
A promising oxygen permeable membrane should not only possess good oxygen permeation flux, but it should also have good stability. The oxygen permeation flux through the acid etched followed by LSC coated PLNCG hollow fiber membrane as a function of time at 800 °C is shown in Fig. 9. During the first 50 h of operation, the membrane exhibits an initial reduction in the oxygen permeation flux, but it should also have good stability, especially at relatively low temperatures. The acid etching can help to give a larger membrane area with rough surface and it will promote the contacting of the coating layer. The key factor for enhancing the oxygen permeation flux is the porous catalytic LSC layer coating on the membrane surface. However, both of these surface modifications are beneficial for improving the oxygen permeation. It has to be admitted that the membrane cannot be used for industrial application based on such low oxygen permeation fluxes measured under air/He gradient, even after surface modification. However, in the reaction of oxygen combustion or partial oxidation of methane (POM), etc., the sweep helium gas will be replaced by methane (or some other fuel, hydrocarbons) which can provide even lower oxygen partial pressure on one side of membrane and resulted in even higher oxygen permeation flux.

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