Oxygen Separation through U-Shaped Hollow Fiber Membrane Using Pure CO2 as Sweep Gas

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A number of U-shaped K2NiF4-type oxide hollow fiber membranes based on (Pr0.9La0.1)2(Ni0.74Cu0.21Ga0.05)O4+δ (PLNCG) were successfully prepared by a phase inversion spinning process. The PLNCG hollow fiber membranes were then used to investigate the effect of CO2 concentration in both the sweep gas and the feed air on the oxygen permeation flux. With pure CO2 as the sweep gas and even 10% CO2 in the feed air, a steady oxygen permeation flux of 0.9 mL/min cm2 (STP) is obtained at 975°C during 310 h, and no decline of the oxygen permeation flux is observed. XRD, SEM and EDS characterizations show the spent membrane still maintains the intact microstructure and perfect K2NiF4-type phase structure without carbonate, which indicates that the U-shaped PLNCG hollow fiber membrane is a very stable membrane under CO2 atmosphere and has great potential for the practical application in oxyfuel techniques for CO2 capture and storage. © 2011 American Institute of Chemical Engineers AIChE J, 58: 2856–2864, 2012

Keywords: hollow fiber, membrane, oxygen permeation, CO2, mixed conductor

Introduction

The atmospheric CO2 concentration has steadily increased from 280 ppm to its current value of 385 ppm since the industrial revolution, representing an increase of 35%. It is mainly due to the unabated emission of CO2 from the consumption of fossil fuels such as coal, oil and natural gas. Around the world, coal combustion is responsible for 42% of the CO2 emission as providing 41% of the electricity. Therefore, CO2 capture and storage technologies (CCS) used to reduce the CO2 emission from coal-fired power plants have gained increasing attentions. Currently, there are mainly three methods for CO2 sequestration: precombustion separation, postcombustion capture and oxyfuel combustion techniques. Recently, mixed conducting ceramic membranes with oxygen ionic and electronic conductivity have attracted increasing attentions due to their potential applications in oxygen supplying for power stations with CO2 sequestration according to the oxyfuel concept. In the oxyfuel process, oxygen diluted with recycled CO2 is used to burn fossil fuels, resulting in a flue gas mainly consisted of CO2 and H2O which can be separated easily with condensation. For this reason, the mixed conducting oxygen permeable membrane used in oxyfuel process should not only have good oxygen permeability, but also good stability especially under atmosphere with high concentration of CO2.

Most studies of mixed conducting oxygen permeable membrane have been concentrated on the perovskite-type oxides which have relatively high-oxygen permeation fluxes. Unfortunately, most of the perovskite material are quite sensitive to CO2. The membranes containing alkaline-earth elements such as Ba and Sr tend to react with acidic gas CO2 to form carbonates. Several groups found that the oxygen permeation fluxes through the perovskite membranes containing alkaline-earth elements had a serious decrease due to the formation of carbonate layer even when a very low concentration of CO2 was added to the sweep gas. It was also found that CO2 in the feed air has a significant effect on the oxygen permeation fluxes through the perovskite membranes containing alkaline-earth elements such as BaCo0.8Fe0.2O3-δ, Sr0.95Co0.8Fe0.2O3-δ and Ba0.5Sr0.5Co0.8Fe0.2O3-δ (BSCF) membranes. Jin et al. also found the lifetime of perovskite membrane reactor which coupled the thermal decomposition of CO2 with the POM reaction was not more than 40 h.

Therefore, intensive efforts have been made to develop the CO2-tolerant mixed conducting oxides. It is reported that the stability in the CO2-containing atmosphere can be improved by proper doping such as Zr-doped BaCe0.8Y0.2O3-δ (BCY) and Ti-doped SrCo0.8Fe0.2O3-δ. On the other hand, A-site-deficient perovskite oxides, such as La0.25Sr0.75Co0.41Fe0.59O1.95 and La0.85Ce0.1Ga0.05Fe0.05Al0.95O3-δ were also found to possess an enhanced resistance against the corrosion of CO2. Recently, Luo et al. developed a novel cobalt-free dual phase CO2-tolerated oxygen permeable membrane. However, most of those aforementioned material were just tested in a low CO2 concentration atmosphere, and the oxygen permeation fluxes decreased significantly once pure CO2 was used as the sweep gas.

In the power plant concept with CO2 sequestration, a part of the effluent gas is used as sweep gas, i.e., the sweep gas for the oxygen separator is consisted of about 80 vol % CO2. This concept requires CO2 resistant membranes without Ba and Sr, like doped La-Ni oxides. Recently,
Yashima et al.44 investigated the oxygen permeability, electrical properties and detailed crystal structure of $K_2NiF_4$-type $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_4$ (PLNCG). It can be expected that the PLNCG should exhibit good resistance to CO$_2$ because it is alkaline-earth elements free membrane. In our previous work, we found that this material has a good stability in CO$_2$-containing atomosphere. In this work, the PLNCG powder. To summarize, Ga was dissolved in nitric acid first, and proper amounts of Pr(NO$_3$)$_3$ and tap water were used as the internal and external coagulants, respectively. Afterwards, 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. The preparation conditions are summarized in Table 1.

The phase structure of the as-prepared PLNCG powder, the fresh hollow fiber membrane after sintering at 1300°C and the spent hollow fiber membrane was characterized by X-ray diffraction (XRD, Bruker-D8 ADVANCE, Cu K$_\alpha$ radiation). The microstructure and morphology of the fresh and spent PLNCG hollow fiber were observed by a scanning electron microscope (SEM, JEOL JSM-6490LA). The oxygen permeation fluxes through the U-shaped PLNCG hollow fiber membranes under CO$_2$-containing atmosphere were investigated in a high-temperature permeation cell, as shown in Figure 1. The effective membrane area in this experiment is 1.2 cm$^2$. The U-shaped PLNCG hollow fiber membrane was sealed in a corundum tube with two channels by a commercial ceramic sealant (HT767, Hutian, China) as shown in Figure 2B. Air or a mixture of CO$_2$, O$_2$ and N$_2$ was fed to the shell side while He or CO$_2$ or a mixture of He and CO$_2$ swept on the core side to collect the permeated oxygen through the membrane. Helium is used for comparison in order to check how CO$_2$ is going to affect the flux. The gas-flow rates were controlled by mass-flow controllers (MFC, Seven Star D08-4F/2M) calibrated using a soap bubble flow meter. The composition of the permeated gases were 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. Assuming that the leakage of nitrogen and oxygen through pores or cracks is in accordance with Knudsen diffusion, the fluxes of leaked N$_2$ and O$_2$ are related by

$$K = J_{N_2}^{\text{leak}} : J_{O_2}^{\text{leak}} = \sqrt{32/28} \times \frac{C_{\text{feed}}^{N_2}}{C_{\text{feed}}^{O_2}}.$$  \hspace{1cm} (1)

The O$_2$ permeation flux was then calculated as follows

$$J_{O_2}(\text{ml/min m}^2) = \left[ C_{\text{cor}}^{O_2} - C_{\text{cor}}^{N_2} \right] \frac{F}{S} \cdot K.$$ \hspace{1cm} (2)

Table 1. Preparation Conditions for the U-shaped PLNCG Hollow Fiber Membranes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinning temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Injection rate of internal coagulant</td>
<td>2.8 ml/min</td>
</tr>
<tr>
<td>Spinning pressure</td>
<td>0.05 bar</td>
</tr>
<tr>
<td>Air gap</td>
<td>0.5 cm</td>
</tr>
<tr>
<td>Sintering temperature</td>
<td>1300 °C</td>
</tr>
<tr>
<td>Sintering time</td>
<td>3 h</td>
</tr>
<tr>
<td>Air flow rate for sintering</td>
<td>60 ml/min</td>
</tr>
</tbody>
</table>

Figure 1. Oxygen permeation apparatus for the U-shaped PLNCG hollow fiber membrane at high temperature.
Where \( C_{\text{feed}} \), \( C_{\text{feed}} \), \( C_{\text{core}} \), \( C_{\text{core}} \) are the oxygen concentration and nitrogen concentration on the shell side, which are adjusted by mass-flow controllers \( C_{\text{core}} \), \( C_{\text{core}} \) are the oxygen concentration and nitrogen concentration on the core side, which are calculated from the GC measurements. \( F \) is the flow rate of the exhaust stream, which can be measured by the soap flow meter, and \( S \) is the hollow fiber membrane effective area.

**Results and Discussion**

Figure 2A shows the photo of U-shaped PLNCG hollow fiber membranes after sintering at 1300°C for 3 h. The SEM micrographs of the cross section, and the wall of the sintered hollow fiber membrane are also shown in Figure 2C and D. The finger-like structures can be observed in the micrographs of PLNCG hollow fiber membranes.

The effects of CO \(_2\) concentration in the sweep gas and the feed air, the flow rate of pure CO \(_2\) (as the sweep gas) on the oxygen permeation flux through the U-shaped PLNCG hollow fiber membrane are investigated at different temperatures. The reversibility and stability of oxygen permeation flux under air/CO\(_2\) gradient are also been studied this work.

Figure 3 presents the effects of CO \(_2\) concentration in the sweep gas on the oxygen permeation fluxes through the U-shaped PLNCG hollow fiber membrane at different temperatures. The flow rate of sweep gas was 60 mL/min (STP) on the core side. It can be seen from Figure 3 that the oxygen permeation flux increases with increasing temperature because both of the oxygen surface exchange and bulk diffusion are improved at high temperatures. When CO \(_2\) is introduced into the sweep gas, the oxygen permeation fluxes only decrease slightly. The oxygen permeation flux through the PLNCG hollow fiber membrane only decreases from 0.98 mL/min.cm\(^2\) (STP) under Air/He gradient to 0.92 mL/min.cm\(^2\) (STP) under Air/CO\(_2\) gradient when the sweep gas flow rate is 60 mL/min (STP) at 975°C. In other words, when the pure CO \(_2\) is used as the sweep gas instead of pure He, only 6.1% decrease of oxygen permeation flux is observed at a flow rate of 60 mL/min (STP) on the core side. The decrease of oxygen permeation flux when switching the sweep gas from He to CO \(_2\) is due to the adsorption of CO \(_2\) on the membrane surface, and decreases the oxygen exchange rate. The effect is more noticeable at low temperature. A decrease around 7.7% of the oxygen permeation flux is observed when temperature decreases from 975 to 950°C. Similar results were also found by other researchers. It also can be observed in Figure 3B that the oxygen permeation fluxes through the PLNCG hollow fiber membrane only slightly change with varying concentration of CO \(_2\) on the core side at different temperatures.

Figure 4 shows the dependence of the oxygen permeation flux on the flow rate of sweep CO \(_2\) at different temperatures. Obviously, even when the pure CO \(_2\) is used as the sweep gas, the oxygen permeation fluxes increase with the increasing sweep CO \(_2\) flow rates. This is attributed to the higher flow rate sweep gas dilutes the permeated oxygen concentration and lowers the oxygen partial pressure on the core side, which leads to a higher oxygen permeation driving force. Moreover, the oxygen permeation flux is more sensitive to the effect of CO \(_2\) flow rate at high temperatures. When the CO \(_2\) flow rate was increased from 15 to 60 mL/min (STP), the oxygen permeation fluxes increases from 0.65 to 0.92 mL/min.cm\(^2\) (STP) and 0.14 to 0.17 mL/min.cm\(^2\) (STP) at 975 and 850°C, respectively. It also can be noted from Figure 4B that the gaps of corresponding permeated oxygen permeation fluxes under different CO \(_2\) flow rate at high temperatures are bigger than that at low temperatures, i.e., the oxygen permeation flux is more sensitive to the effect of the CO \(_2\) flow rate on the core side at high temperatures than that at low temperatures. In fact, it is unpracticised using such a big sweep gas flow to get oxygen in practice. For the oxyfuel combustion based on the oxygen permeable membrane, the required sweep gas flow is related to the effective membrane area and the oxygen permeation flux, which can make the oxygen concentration higher than 20%, i.e., the fossil fuels can combust in an oxygen-enriched air compared with the ordinary air. In the corresponding Arrhenius plot (shown in
Therefore, the effects of CO₂ concentration in the feed air on the oxygen permeation fluxes through the U-shaped PLNCG hollow fiber membrane at different temperatures is investigated here. In this experiment, the oxygen partial pressure on the shell side keeps 0.21 atm, and the CO₂ concentration is controlled by adjusting the ratio of N₂ and CO₂. As shown in Figure 7, when the concentration of CO₂ in the feed air increases from 0 to 60%, the oxygen permeation flux maintains the initial oxygen permeation flux at temperatures from 850 to 950°C. Only at a higher temperature, such as 975°C, a slight decrease of the oxygen permeation flux is observed. The oxygen permeation flux through the PLNCG hollow fiber membrane changes from 0.94 mL/min/cm² (STP) to 0.93 mL/min/cm² (STP) when the CO₂ concentration in the feed air increases from 0 to 10% CO₂ at 975°C. Afterward, with the increase of CO₂ content in the feed air, the oxygen permeation fluxes are almost constant, which indicates PLNCG is really a kind of CO₂-stable material. It can also be found in Figure 7B that the oxygen permeation fluxes through the PLNCG hollow fiber membrane maintain a constant value with varying CO₂ concentration in the feed air at each temperature. However, Park et al. found the oxygen permeation flux through BSCF disk membrane decreased from 1.4 to 0.8 mL/min/cm² when 700 ppm (0.07%) CO₂ was introduced into the feed air at 950°C, nearly 43% decrease of oxygen permeation flux was observed. Tong et al. also found the oxygen permeation flux through BaCo₀.₄Fe₀.₄Zr₀.₂O₃-disk membrane decreased from 0.88 to 0.79 mL/min/cm² when 10% CO₂ was introduced into the feed air at 950°C. Compared to these material, the effect of
CO₂ in the feed air on the oxygen permeation flux through PLNGC hollow fiber membrane is negligible and PLNGC exhibits a good stability under CO₂ atmosphere.

Figure 8 presents the oxygen permeation fluxes through the U-shaped PLNGC and BSCF hollow fiber membranes with different CO₂ concentration in the sweep gas on the core side. As known, BSCF is a good membrane but chemically less stable among many perovskite materials. The oxygen permeation flux through the U-shaped BSCF hollow fiber membrane at 950°C is above 4.0 mL/min/cm² (STP) under air/He gradient. However, the oxygen permeation flux through the BSCF hollow fiber membrane sharply drops to 1.4 mL/min/cm² (STP) when 20% CO₂ is added to the sweep gas. Furthermore, it decreases gradually with time when a mixture of 20% CO₂ and 80% He was used as the sweep gas. After 2 h operation, the oxygen permeation flux declines to 1.0 mL/min/cm² (STP), which is only 25% of the initial oxygen permeation flux when using pure He as the sweep gas. When the CO₂ concentration in the sweep gas increases to 40%, the oxygen permeation flux through the BSCF hollow fiber membrane declines to only 0.2 mL/min/cm² (STP). An immediate stop of the oxygen permeation flux through the BSCF hollow fiber membrane is observed when pure CO₂ is used as the sweep gas, which has also been found in the disk membrane by Arnold et al.

It is known that the alkaline-earth metal ions of Ba and Sr on the A site of perovskite structure are sensitive to CO₂ and tend to react with CO₂ to form carbonate, which leads to the decrease of oxygen permeation flux. Compared with BSCF, the oxygen permeation flux through the U-shaped PLNGC hollow fiber membrane is much stable under different CO₂ concentrations (from 0 to 100%) in the sweep gas on the core side. Although the oxygen permeation flux through the PLNGC hollow fiber membrane is not as high as that through BSCF hollow fiber membrane when pure He is used as the sweep gas, it keeps the initial oxygen permeation flux of around 1.0 mL/min/cm² (STP) all the time even when the pure CO₂ was used as the sweep gas. The results demonstrate that PLNGC shows much better CO₂-tolerable property than the perovskite containing alkaline-earth metal. The possible reason is that there is no alkaline-earth metal element in such a K₂NiF₄-type material.

Figure 9A shows the oxygen permeation flux as a function of time through the PLNGC hollow fiber membrane using pure CO₂ as the sweep gas at 975°C. During this oxygen permeation test, a steady oxygen permeation flux of about 0.9 mL/min/cm² (STP) is obtained at 975°C with the CO₂ sweep-flow rate of 60 mL/min (STP), and the oxygen concentration of the down stream kept around 1.8 kPa. The oxygen permeation flux keeps constant even after 310 h and no decrease is observed. Many literatures have reported that the oxygen permeation fluxes through oxygen permeable membranes decreased sharply when the CO₂ was introduced into either the sweep gas or the feed air.

It was found that the oxygen permeation flux through BSCF membranes decreases rapidly once CO₂ gas is introduced into the sweep side. It was also noted that when CO₂ was added in the feed air on the shell side, the oxygen permeation fluxes through BaCo₁₀₋₄Fe₀.₄Zr₀.₂O₃₋₅, Sr₀.₉Co₀.₁Fe₀.₉O₃₋₅ and BSCF membranes decreased due to the instability of these membranes in CO₂-containing atmosphere. Therefore, it can be presumed that the oxygen permeation flux will have a rather bigger decrease if CO₂ exists in both the sweep gas and the feed air. In order to examine the stability of the PLNGC hollow fiber membrane in a more rigorous condition, the oxygen permeation flux through the PLNGC membrane is investigated when both the sweep gas and the feed air contains CO₂, as shown in Figure 9B. In this experiment, the pure CO₂ with the flow rate of 60 mL/min (STP) is used as the sweep gas on the core side, while 4 and 10% CO₂ is introduced into the feed air, respectively. As shown in Figure 9A, during the 310 h oxygen permeation test, the oxygen permeation flux keeps constant even though CO₂ exists simultaneously on the both sides of the hollow fiber membrane, which indicates the good stability of PLNGC under CO₂-containing atmosphere. Compared with these CO₂-sensitive material mentioned previously, PLNGC exhibits excellent CO₂ tolerance.

After the 310 h oxygen permeation test through the U-shaped PLNGC hollow fiber membrane at 975°C, the sample is characterized by XRD, SEM and EDS. Figure 10 presents the phase structures of the PLNGC powder prepared by a combined EDTA-citrate complexation, the fresh hollow fiber membrane sintered at 1300°C and the spent hollow fiber membrane after 310 h oxygen permeation with pure CO₂ as the sweep gas and CO₂-containing air as the feed gas (Figure 9). The X-ray diffraction patterns indicate all of them are pure K₂NiF₄-type structure. Furthermore, after the 310
h’ oxygen permeation operation, no carbonate is observed which indicates that the U-shaped PLNCG hollow fiber membrane exhibits excellent phase structure stability under CO2 atmospheres.

Figure 11 also shows the SEM micrographs of the fresh and spent PLNCG hollow fiber membrane after 310 h’ permeation test in CO2 containing atmosphere. Figure 11A and B shows the inner and outer surface of the fresh PLNCG hollow fiber membrane. The particles on both the inner and outer surfaces in this K2NiF4-type PLNCG system looks like aciculate and it can be noted that the PLNCG particles connect to each other firmly.

Figure 9. (A) Long-term operation of the oxygen permeation through the U-shaped PLNCG hollow fiber membrane with pure CO2 as the sweep gas at 975 °C. Conditions: FN2 + O2 + CO2 = 180 mL/min, FCO2 = 60 mL/min, CO2 concentration in the feed gas kept 0% for 160 h, 4% for 100 h and 10% for 50 h, respectively, and (B) Model of the oxygen separation through the PLNCG hollow fiber membrane swept by pure CO2.

Figure 8. Oxygen permeation fluxes through the U-shaped BSCF and PLNCG hollow fiber membrane with different CO2 concentration in the sweep gas.

Conditions: CO2 concentration in the sweep gas varied from 0 to 100%; BSCF: T = 950 °C, Fair = 150 mL/min, Fsweep = 100 mL/min; PLNCG: T = 975 °C, Fair = 180 mL/min, Fsweep = 60 mL/min.

Figure 10. XRD patterns of the PLNCG powder, fresh and spent hollow fiber membrane after 310 h’ operation (in Figure 9).
of the inner surface keeps intact and no carbon was detected by EDS. The impurity on the outer surface exposed to the air of the spent hollow fiber membrane contains Al and Si, which was detected by EDS. They are from the decomposition of the ceramic sealant. In summary, both of the inner and outer surfaces of the spent PLNCG hollow fiber membrane keeps intact and the PLNCG particles still connect to each other firmly.

Table 2 summarizes the CO₂ effect on the oxygen permeation fluxes through various membranes based on different mixed conducting oxides. As shown in Table 2, when the membrane is exposed to a CO₂-containing atmosphere or even pure CO₂ atmosphere, the decreases of the oxygen permeation fluxes through most of the membranes are more than 90%, such as BSCF. It is because these membranes contain alkaline-earth metals, which tend to react with CO₂. On the other hand, carbonate appears in most phase structures after these membranes exposed to CO₂-containing atmosphere. However, the situation is much better in alkaline-earth metal-free systems, such as La₀.₈₅Ce₀.₁Ga₀.₃Fe₀.₆₅Al₀.₀₅O₃₋₄, 40%NiFe₂O₄ – 60%Ce₀.₉Gd₀.₁O₂₋₄ and PLNCG listed in Table 2. The decreases of the oxygen permeation fluxes through these membranes are not only less than 40%, the phase structures also keep their initial structure-types without carbonate. Among these three alkaline-earth metal-free membranes, the PLNCG hollow fiber membrane investigated in present work exhibits excellent performance. The decrease of the oxygen permeation flux through the PLNCG hollow fiber membrane is only 6% at 975°C, which is the least one among all these mixed conducting oxides reported. Furthermore, the operation time of oxygen separation through the U-shaped PLNCG hollow fiber membrane swept by pure CO₂ is more than 310 h, which is the longest one reported and the feed gas also contains CO₂ simultaneously. The constant oxygen permeation flux through the PLNCG membrane in such a rigorous conditions indicates the excellent phase stability of the U-shaped PLNCG hollow fiber membrane.

All these above results demonstrate that the U-shaped PLNCG hollow fiber membrane exhibits good oxygen permeability and excellent phase stability under CO₂-containing atmosphere, which indicates its potential applications in the oxyfuel techniques and CO₂ capture process.

**Conclusion**

The U-shaped K₂NiF₄-type oxide hollow fiber membranes based on (Pr₀.₉La₀.₁)₂(Ni₀.₇₄Cu₀.₂₁Ga₀.₀₅)O₄+(PLNCG) are successfully prepared by a phase inversion spinning process. The effects of CO₂ concentration in the sweep gas and the feed gas, as well as the flow rate of pure CO₂ as the sweep gas on the oxygen permeation flux through the PLNCG hollow fiber membrane at different temperatures are investigated in detail. Compared with the oxygen permeation flux under Air/He gradient, the most serious decrease of oxygen

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**Table 2. Comparison of the CO₂ Effect on the Oxygen Permeation Fluxes Through the Membranes Based on Different Mixed Conducting Oxides**

<table>
<thead>
<tr>
<th>Material</th>
<th>T / °C</th>
<th>Sweep gas</th>
<th>J₀₂ decrease</th>
<th>Phase structure after exposure</th>
<th>Lifetime</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₀.₈₅Ce₀.₁Ga₀.₃Fe₀.₆₅Al₀.₀₅O₃₋₄</td>
<td>950</td>
<td>20%CO₂+80%He</td>
<td>37%</td>
<td>No obvious degradation</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>BaCoₓFe₉₋ₓZr_xO₁₉₋ₓ (x+y+z=1)</td>
<td>900</td>
<td>20%CO₂+80%He</td>
<td>93%</td>
<td>BaCO₃</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>BaCoₓFe₉₋ₓNb_xO₁₉₋ₓ</td>
<td>900</td>
<td>pure CO₂</td>
<td>93%</td>
<td>BaCO₃, CoO</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Ba₀.₆SrₓCo₀.₄FeₓO₄₋₄</td>
<td>875</td>
<td>pure CO₂</td>
<td>97%</td>
<td>(Ba₀.₆Srₓ)CO₃, CoO</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Ba₀.₆SrₓFe₀.₄ZnₓO₄₋₄</td>
<td>750</td>
<td>pure CO₂</td>
<td>100%</td>
<td>(Ba₀.₄Srₓ)CO₃, ZnO</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>40%NiFe₂O₄ – 60%Ce₀.₉Gd₀.₁O₂₋₄</td>
<td>1000</td>
<td>pure CO₂</td>
<td>10%</td>
<td>No carbonate</td>
<td>&gt;100 h</td>
<td>41</td>
</tr>
<tr>
<td>PLNCG</td>
<td>975</td>
<td>pure CO₂</td>
<td>6%</td>
<td>No carbonate</td>
<td>&gt;310 h</td>
<td>This work</td>
</tr>
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</table>
permeation flux is only 6% when pure CO₂ is used as the sweep gas on the core side. When the pure CO₂ is used as the sweep gas and even 10% CO₂ was added in the feed air simultaneously, a steady oxygen permeation flux of 0.9 mL/min cm² (STP) is obtained at 975°C and no decline of the oxygen permeation flux is observed. XRD, SEM and EDS characterizations indicate that the spent membrane still maintains the perfect K₂NiF₄-type phase structure and intact microstructure without carbonate. All of these results demonstrate that the U-shaped PLNGC hollow fiber membrane is a promising stable membrane under CO₂-containing atmosphere and has a great potential for the practical application in oxyfuel techniques for CO₂ capture and storage technologies.

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