

Dual Phase Membrane for High temperature CO₂ Separation

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Jerry Y.S. Lin
Seungjoon Chung

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Department of Chemical & Material Engineering
University of Cincinnati
Cincinnati, OH 45221-0171

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ABSTRACT

This project is aimed at synthesis of a new inorganic dual-phase carbonate membrane for high temperature CO₂ separation. Metal-carbonate dual-phase membranes were prepared by the direct infiltration method and the synthesis conditions were optimized. The dual-phase membranes are gas-tight with helium permeance about six orders of magnitude lower than that for the metal support. Efforts were made to test seals for permeation and separation experiments for dual-phase membrane at the intermediate temperature range (about 500°C) under oxidizing atmosphere. An effective new permeation cell with a metal seal was designed, fabricated and tested. The permeation setup provided leak-free sealing for the dual-phase membranes under the desired operation conditions. Though the reliable data showing high permeance for carbon dioxide with oxygen for the prepared metal-carbonate dual phase membrane has not been measured, the research efforts in improving membrane synthesis and setting up a new permeation cell with suitable seal have made it closer for one to demonstrate good dual-phase membranes for high temperature carbon dioxide separation.

Research efforts were also directed towards preparation of a new ceramic-carbonate dual-phase membrane. Porous lanthanum cobaltite (LC) perovskite type oxide ceramic support with oxidation resistance better than the metal support and high electronic conductivity (1300-1500 S/cm in 400-600°C), was prepared and studied as an alternative support for the dual-phase carbonate membranes. The LC powder was found not reactive with the carbonate at 600°C. The porous LC disks have helium permeance and pore diameter smaller than the metal support but larger than the common α -alumina support. These results show promise to use the LC support for preparation of oxidation resistant dual-phase carbonate membranes.

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INTRODUCTION

Extensive research has been done in the past decade on microporous inorganic membrane for carbon dioxide separation. However, microporous inorganic membranes only give high selectivity at low temperatures but not at high temperatures ($>350^{\circ}\text{C}$). Therefore, dense inorganic membrane has been a focus of recent studies for high temperature separation purposes [1]. It is known that molten carbonate, such as $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$, can conduct CO_3^{2-} at a very high rate. This is the basis of the molten carbonate fuel cell (MCFC). We proposed a dual phase metal-carbonate dense membrane for high temperature CO_2 separation. This membrane consists of a porous metal phase and a molten carbonate phase, as shown in Figure 1. The metal phase not only serves as a support but also transports electrons. Carbon dioxide separation can be accomplished with the driving force of the CO_2 partial pressure gradient. On the upper stream membrane surface CO_2 , combining with electrons and oxygen, formed CO_3^{2-} , which transports through the molten carbonate phase. The CO_3^{2-} releases electrons to form CO_2 and O_2 on the downstream membrane surface. The electron transports back, through the metal phase, towards the upstream membrane surface. No external electrodes and connector are required in this dual phase membrane. Since only carbon dioxide (with oxygen) can transport through the molten carbonate, the selectivity for CO_2 over nitrogen or other gases is theoretically infinite.

The dual-phase metal-carbonate membrane is an extension of the fuel cell concept. This follows the similar approach the inorganic membranologists used for making dense mixed-conducting ceramic membranes for oxygen separation, also extended from the concept of the solid oxide fuel cell. The major uncertainty for the successful development of this dual-phase membrane was whether a hermetic, stable metal-carbonate dual phase membrane could be fabricated by the direct infiltration

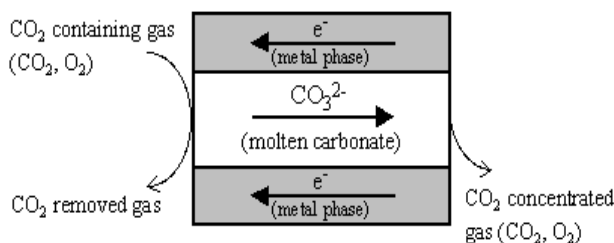


Figure 1. Membrane Wall Cross-Sectional View
Illustrating the Concept of Dual Phase Metal-Carbonate
Membrane for High Temperature CO_2 Separation

method and the metal and carbonate phases could provide continuous, effective pathways for transport for carbeneous ions and electrons. The research activities conducted in the first year were to prepare the gas-tight metal-carbonate dual phase membrane and set up reliable permeation system with adequate seal for characterizing the membranes in the intermediate temperature range under oxidizing atmosphere. We also extended the dual-phase membrane concept to ceramic-carbonate membranes for improved oxidation resistance. Along this direction, we started research to prepare porous,

electrically conducting perovskite type ceramic supports, which will be used as the electronically conducting phase for oxidation resistance ceramic-carbonate dual-phase membranes for high temperature separation of carbon dioxide.

EXPERIMENTAL

Preparation of Metal-Carbonate Membrane

Mixture of 43.5/31.5/25 mol% of Li/Na/K, instead of Li/Na, carbonates was used as molten carbonate phase (melting point 397°C). Porous metal membranes provided by Mott Corporation (sphere particle compacted) were used to hold carbonate inside the pores. Metal membrane media grade 0.5 membrane (average particle size of 0.5 μm) was chosen because, as compared to others metal membranes (media grade 1, 2, 5, 10), it has the smallest pore size (about 400 nm) so the molten carbonate can be stabilized in the pores due to the capillary pressure. Metal-carbonate membrane was prepared by a simple dip-coating procedure as schematically illustrated in Figure 2. Dual-phase membranes were prepared with different preheating conditions, contact time, and temperature of carbonate to identify the optimum conditions. A carbonate overlayer often covered the surface of the membranes after dip-coating. This overlayer might cause sealing failure and carbon dioxide not to pass in the forms of CO_3^{2-} ion during the subsequent permeation/separation tests. In this case the dual-phase membranes with overlayer of molten carbonate (prepared at lower temperature) were polished with sandpaper (Scotch Brite®) by hands to remove the overlayer.

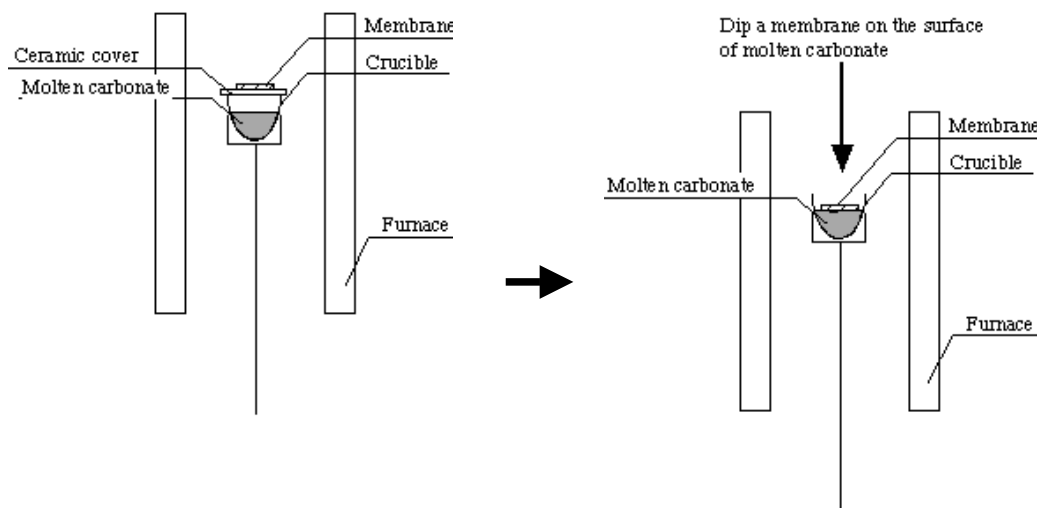


Figure 2. Preparation step for dual-phase membrane

Metal-carbonate membrane was characterized with various gases by the unsteady-state permeation setup shown in Figure 3. He Permeance was measured to examine the gas-tightness of the membrane. CO₂ and N₂ permeation fluxes were also measured at different temperatures. Permeation of CO₂ with oxygen was the critical step to verify electron-ion conducting mechanism. Mean pore diameter of the porous membrane support was characterized by the steady-state permeation setup as shown in Figure 4.

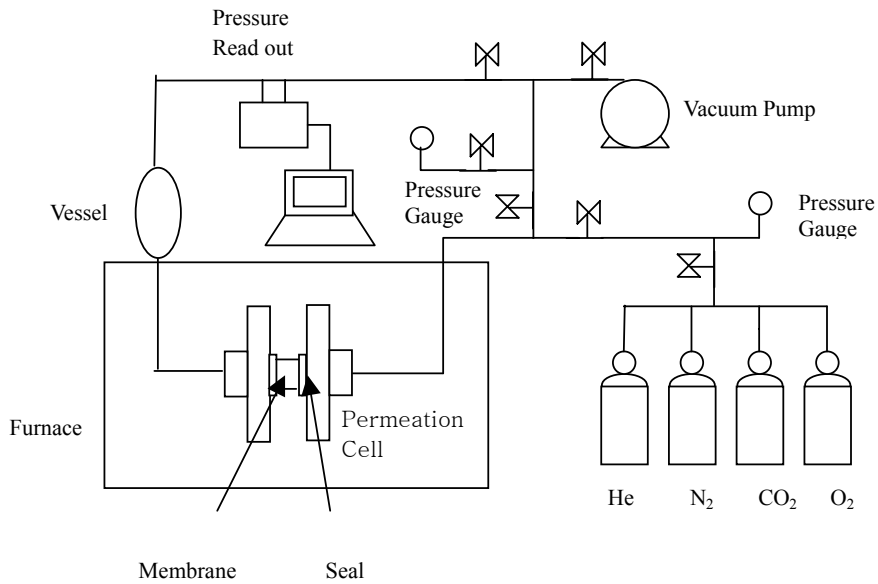


Figure. 3. Schematic Diagram of unsteady state permeation setup to measure permeance

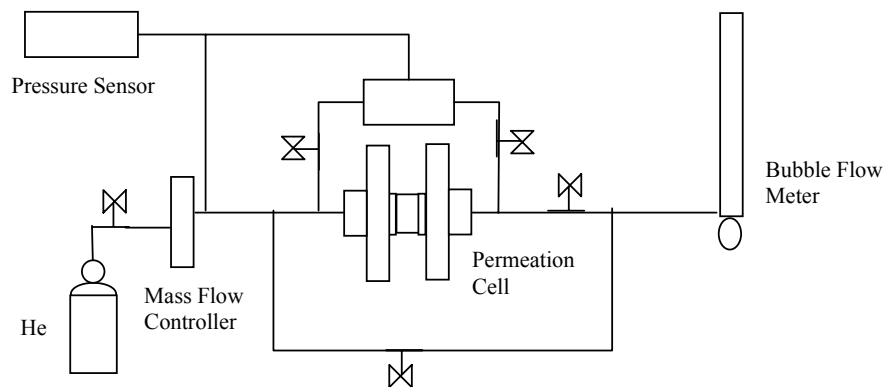


Figure 4. Schematic diagram of steady state helium permeation

Permeation Cell and Seal Design

Sealing membranes for experiments in 400-600°C under oxidizing atmosphere is a challenging problem. Various kind of seal materials, summarized in Table 1, were tested for the high temperature permeation cell. Conventional Rubber O-ring was used to verify gas-tightness obtained during coating procedure because rubber O-ring shows best sealability at room temperature. Graphite shows both good compressibility and temperature resistance, but it would be oxidized with oxygen around operating temperature (450-500°C). Metal seals were also tested because it was easier to work with them.

Table 1. Seal material used for permeation cell

Seal material	Rubber	Graphite	Nickel Alloy	Silver	Gold
Maximum Temperature (°C)	200-300	450(oxygen) 3000(steam)	982	962	1063
Thermal expansion coefficient (10 ⁻⁶ /°C)	-	-	-	15.2	20.6

A new permeation cell with improved oxidation resistance and sealability was designed and fabricated. The permeation cell and connections were made out of 316LSS stainless steel of oxidation resistance grade. Inner chamber was fit to the sample size (19.05mm) to get gas-tightness. Flexible pure graphite gasket was used to seal the outside chamber not in contact with permeation gas (oxygen). Noble metal ring (gold / silver) which is soft and oxidation resistant was installed to seal the inside chamber.

Table 2. Conditions for the preparation of LC by the citrate method

Step	Details
Precursors	La(NO ₃) ₃ .6H ₂ O, Co (NO ₃) ₂ , Co(NO ₃) ₃ .6H ₂ O
Polymerization	100-105°C, stirring, 5h
Condensation	100-105°C
Powder Drying	110°C
Self Ignition Step	400°C, 1hr
Preliminary Sintering	600°C, 5-24hr
Disc Pressing	15000-20000lb / 22mm dia.
Final Sintering	900°C, 20hr, Ramping Rate 2° C/min

Ceramic-Carbonate Membrane

As an alternative material for metal substrate, porous lanthanum-cobaltite (LC) perovskite ceramic was considered as the holding (or electronic conducting) phase because it has high electronic conductivity (1200-1500 S/cm) at the temperature range of interest (400-600°C). The composition of LC material was chosen as ratio of La:B:Co:C = 6:4:8:2 (where B and C are dopants). The citrate method [3] was used to prepare the porous LC support. Several testing experiments have been done to modify preparation procedure with XRD and DSC-TGA analysis. Detailed procedure and conditions to fabricate the porous LC support are summarized in Table 2. One of the advantages of using this material is our ability to control pore size and capillary force.

RESULTS AND DISCUSSION

Metal-Carbonate Membranes

Gas-tight metal-carbonate membranes could be readily prepared by the method described in the experiments. Helium permeance of the dual-phase membranes was typically around 1×10^{-10} mol/s.m².Pa, 5 to 6 orders of magnitude lower than the helium permeance for the metal support. This gas-tightness was obtained with rubber-O ring as the seal. Table 3 compares gas-tightness of a gas-tight metal-carbonate dual phase membrane with different seals at the room temperature. Rubber O-ring is superior to other seal materials but cannot be used at high temperatures (>300°C). However, rubber O-ring could be used as a standard for comparing the sealability of other seals. As shown in Table 3, except for the pure graphite seal, all other seals tested provided leak-free sealing for the dual-phase membranes at the room temperature.

Table 3. Gas tightness test of dual-phase membrane with various seals at R.T.

Seal	Rubber*	Pure Graphite	Graphite Composite	Nickel Alloy	Silver*
He Permeance (mol/s.m ² .Pa)	$2 \sim 8 \times 10^{-10}$	1×10^{-7}	$8 \sim 9 \times 10^{-9}$	$7 \sim 8 \times 10^{-9}$	6×10^{-10}

* different permeation cell was used

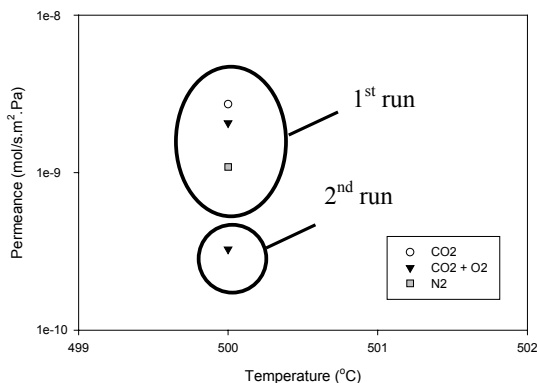


Figure 5. Permeation data with graphite seal at 500°C

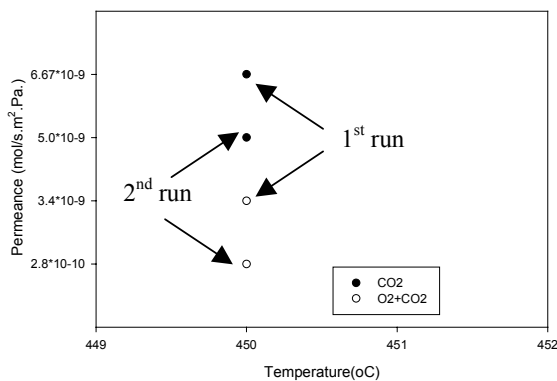


Figure 6. Permeation data with graphite composite seal

Gas-tightness and permeation tests of the dual-phase membranes sealed by these seals were tested with different feed gases at high temperatures (500°C). The results are shown in Figures 5-7. As shown in Fig. 5, the pure graphite (1st run) provided good sealing at the beginning with three different feed gases. After the 1st run tests (tests with the three different gases), the permeance decreased substantially (see 2nd run data). Similar results were also obtained for the graphite composite seal, as shown in Figure 6. After the permeation tests at 500°C, the membrane surface was examined visually. It was found that the membrane surface was contaminated with a red and brown deposit. It was possible that carbon from the graphite seal was vaporized and deposited on the membrane surface and reacted with metal or carbonate. The deposit decreased permeance for all gases.

Gas permeance through the dual-phase membrane with nickel alloy seal is shown in Figure 7. The permeance remained constant at different temperatures after several runs of permeation tests. It also provided fairly good gas-tightness. This suggests that metallic seal should be used for permeation and separation experiments for the dual-phase membranes at high temperatures. However, the dual-phase membranes tested with the results given in Figures 5-7 did not exhibit the expected high permeance for CO₂ with oxygen as the feed. This is due to the formation of a carbonate overlayer and partial oxidation of metal surface, which prevent transport of electrons for the surface charge transfers, as to be discussed next.

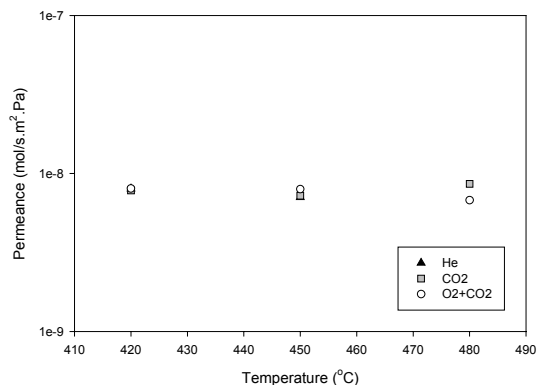


Figure 7. Permeation data with nickel alloy seal at various temperatures (about 450°C)

After dip-coating of metal substrate into molten carbonate, an overlayer of carbonate was often observed on the surface of the dual-phase membrane. The overlayer on the metal-carbonate membrane surface was then sanded off by a Scotch Brite® sanding paper (surface color changed from gold color to the original color), and permeation of carbon dioxide without and with oxygen was measured at about 400°C. Permeance of carbon dioxide without oxygen was 7.8×10^{-9} mol/s.m².Pa. With the presence of oxygen, the carbon dioxide permeance was 6.8×10^{-9} mol/s.m².Pa. Examination of the membrane sample removed from the permeation cell reveals that the membrane surface was

covered with white and yellow particles. XRD analysis shows the presence of impurity phases, possibly iron oxide, on the membrane surface. Electric conductivity measurements show that the membrane was no longer electrically conducting. It was possible that exposure of the dual-phase membrane to the oxygen containing gas at high temperature prior to the permeation measurements with carbon dioxide and oxygen caused oxidation of the metal surface.

Table 4. Single gas permeance data with new permeation cell and silver seal for a dual-phase membrane at two different temperatures

Temperature	N ₂ Permeance	CO ₂ Permeance
25°C	1*10 ⁻⁹	2*10 ⁻⁹
450°C	5*10 ⁻¹⁰	8*10 ⁻⁹

To reduce the thickness of the carbonate overlayer, dual-phase metal carbonate membranes were prepared at different dip-coating temperatures (400-600°C). It was found that the carbonate overlayer can be avoided by dip-coating the metal substrate with the molten carbonate at 600°C for 1-2 sec. The dual-phase membrane obtained under this modified conditions was gas-tight, as confirmed by the nitrogen and pure carbon dioxide permeance using the new permeation cell with silver ring as the seal. The room temperature permeation data are summarized in Table 4. The membrane cell was then heated to 450°C and nitrogen and carbon dioxide permeance were measured at the high temperature. The results are also given in Table 4. Compared to the room temperature permeance data, the nitrogen permeance is lower and carbon dioxide permeance is higher at the high temperature. This suggests that the new cell and silver seal work very well for the dual-phase membranes at the high temperature, and the molten carbonate dual-phase membranes exhibits permselectivity for carbon dioxide (without oxygen) over nitrogen. However, the permeation test with carbon dioxide with oxygen could not be performed on this membrane sample because the molten carbonate was accidentally blown out from the metal support due to experimental errors (too large total transmembrane pressure drop). Research is being continued in the direction to demonstrate high carbon dioxide permeance (with oxygen) for this dual-phase membrane.

Ceramic-Carbonate membrane

As showed, one of the major problems with the metal-carbonate membranes is that the metal support is not oxidation resistant and could be oxidized in carbon dioxide and oxygen. An electronically conducting porous support of perovskite type doped lanthanum cobaltite (LC) is proposed as an alternative electronically conducting phase for the dual-phase membranes. The

perovskite type ceramic support not only conducts electrons at around 500°C but is highly oxidation resistant. In order to realize the concept of the ceramic-carbonate membrane, the reactivity between carbonates and LC ceramics was first checked. LC powder was mixed with Li/Na/K carbonates (43.5/31.5/25 mol %), followed by grinding. The mixture was heated at 600°C overnight, XRD analysis was performed on these samples and the results are shown in Figure 8. As shown, the XRD pattern for the perovskite type phase in the LC-carbonate mixture sample after the heat-treatment is identical to that for the pure perovskite phase. Small peaks around 25-30 and 33-40 degree for the LC-carbonate mixture after the heat-treatment are from the carbonates.

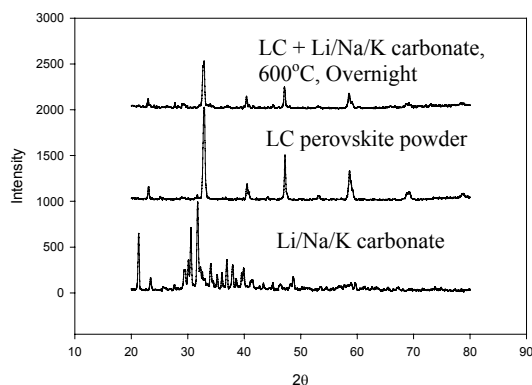


Figure 8. XRD peaks of LC, carbonate, and LC-carbonate mixture after heat-treatment (600°C. overnight)

For the proposed ceramic-carbonate dual-phase membrane, porous LC ceramic disks with different pore size should be prepared. The LC powder used to prepare porous LC disks went through self-combustion at 400°C for 2 hrs and pre-sintering at about 600°C for at least 5 hr. Based on the TGA/DSC analysis of the as-synthesized LC powder, the organic phase was burnt out during the self-combustion at 400°C and the perovskite phase was partially formed after pre-sintering at 600°C for 5 hr. Porous LC discs were prepared by pressing about 2.0g of the pre-sintered LC powder in a die (22.0 mm diameter) up to force of 15,000- 20,000lb for 3 min. These green disks were then sintered at 900°C for 20 h with ramping rate 2.0°C/min. Helium permeance through the porous LC disks was measured by the steady state permeation setup shown in Figure 4. Helium permeance versus average pressure data was used to calculate the average pore diameter [3]. The helium permeance and pore size data for the porous LC support are compared with the metal support used in the metal-carbonate membrane and another common porous support used in our laboratory, α -alumina support. As shown, the LC support has the helium permeance and pore size between those for the metal and alumina supports. It should be noted that the pore size of the LC support can be varied by

using LC powder of different particle size (by varying pre-sintering temperature and time), or changing final sintering temperature and time.

Table 5. Properties of LC and Alumina support

Support	Porous 316LSS (Grade 0.5)	LC	Alumina
He Permeance (mol/s.m ² .Pa)	1.0 x 10 ⁻⁴	1.1 x 10 ⁻⁵	8.0 x 10 ⁻⁶
Average pore diameter (nm)	930	370	240

Final sintering of the green LC membranes at 900°C not only serves the purpose to densify the green disk but also allows completion of phase transformation of LC to the perovskite structure. Fig. 9 compares the XRD patterns of the LC disks before and after the final sintering. As shown, before final sintering the sample contains the perovskite phase as well as other impurity phases. Sample after the final sintering only contains the perovskite phase. Electric conductivity measured by the 2-point DC method shows that LC support before final sintering (after preliminary sintering) is not electronic conducting. It became electronically conducting after final sintering at 900°C for 20h.

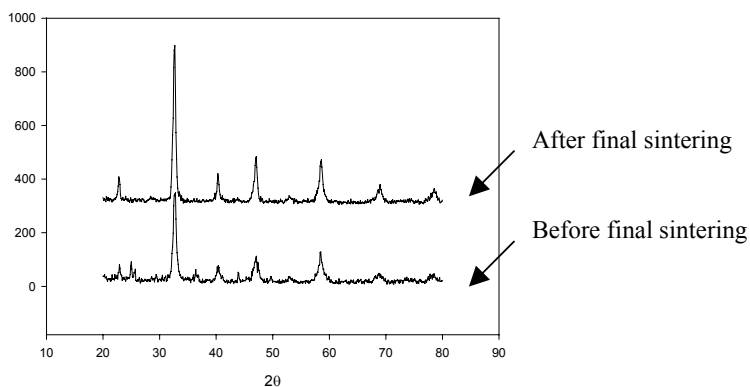


Figure. 9. XRD peaks of LC before and after final sintering (900°C, 20h)

CONCLUSIONS

Metal-carbonate dual-phase membrane was prepared by the direct infiltration method. The dual-phase membranes are gas-tight with helium permeance about six orders of magnitude lower than that for the metal support. A new permeation cell with a metal seal was designed, fabricated and proved to provide leak-free sealing for the dual-phase membranes in the intermediate temperature range (about 500°C) under oxidizing atmosphere (carbon dioxide and oxygen). With the research efforts in improving membrane synthesis and setting up a new permeation cell with suitable seal, we are closer to successful demonstration of good dual-phase membranes for high temperature carbon dioxide separation.

Porous lanthanum cobaltite (LC) perovskite type oxide ceramic support, with better oxidation resistance and high electronic conductivity (1300-1500 S/cm in 400-600°C), was prepared and studied as the alternative support for the dual-phase carbonate membranes. The LC powder was found not reactive with the carbonates at 600°C. LC porous disks have helium permeance and pore diameter smaller than the metal support but larger than the common α -alumina support. These results show promise to use the LC support for preparation of oxidation resistant dual phase carbonate membranes.

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