

Dual Phase Membrane for High temperature CO₂ Separation

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ABSTRACT

Research in the previous years in this project found that stainless steel supports are oxidized during high temperature, dual phase membrane separation of carbon dioxide (with oxygen). Consequently, a new material has been sought to alleviate the problems with oxidation. Lanthanum cobaltite oxide is a suitable candidate for the support material in the dual phase membrane due to its oxidation resistance and electronic conductivity. Porous lanthanum cobaltite membranes were prepared via the citrate method, using nitrate metal precursors as the source of La, Sr, Co and Fe. The material was prepared and ground into a powder, which was subsequently pressed into disks for sintering at 900°C. Conductivity measurements were evaluated using the four-probe DC method. Support pore size was determined by helium permeation.

Conductivity of the lanthanum cobaltite material was found to be at a maximum of 0.1856 S/cm at 550°C. The helium permeance of the lanthanum cobaltite membranes for this research was on the order of 10^{-6} moles/m²·Pa·s, proving that the membranes are porous after sintering at 900°C. The average pore size based on steady state helium permeance measurements was found to be between 0.37 and 0.57 μm. The lanthanum cobaltite membranes have shown to have desired porosity, pore size and electric conductivity as the support for the dual-phase membranes.

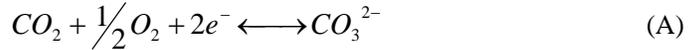
Molten carbonate was infiltrated to the pores of lanthanum cobaltite membranes support. After infiltration with molten carbonate, the helium permeance of the membranes decreased by three orders of magnitude to 10^{-9} moles/m²·Pa·s. This number, however, is one order of magnitude larger than the room temperature permeance of the stainless steel supports after infiltration with molten carbonate. Optimization of the dip coating process with molten carbonate will be evaluated to determine if lower permeance values can be obtained with the lanthanum cobaltite membrane supports.

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INTRODUCTION

Current investigations are underway to develop a stable dual phase membrane for CO₂ separation. Research conducted in the previous years in this project centered on a dual phase membrane that was comprised of porous stainless steel supports infiltrated with a molten carbonate mixture (Li₂CO₃, K₂CO₃, NaCO₃). Metal supports were used because the material can supply electrons to facilitate the reaction that makes the concept of the dual phase membrane possible. CO₂ and O₂ in the presence of an electron rich environment have the tendency to ionize and form CO₃²⁻:



Molten carbonate, which is infiltrated within pores of the support, is a good conductor of CO₃²⁻. Separation is driven by the partial pressure gradient of CO₂ between the up and downstream sides of the membrane. Figure 1 shows how CO₂ can be separated with this concept.

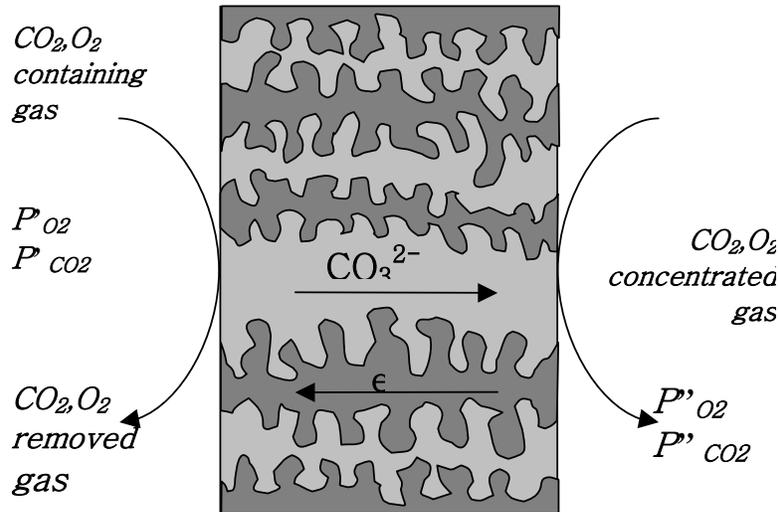


Figure 1 Schematic illustration of the new dual-phase membrane for carbon dioxide separation

Once CO₃²⁻ reaches the downstream side of the membrane, the electrons are released back into the metal support and circulated toward upstream side of the membrane. Accordingly, the CO₃²⁻ ion decomposes on the downstream side to form CO₂ and O₂.

The stainless steel supports that were used before were shown to facilitate the above reaction, but problems arose when CO₂ permeation experiments were conducted at higher temperatures (>650°C). Permeation results for pure N₂, pure CO₂ and a 50%:50% CO₂/O₂ gas mixture were obtained within the temperature range of 450-750°C.

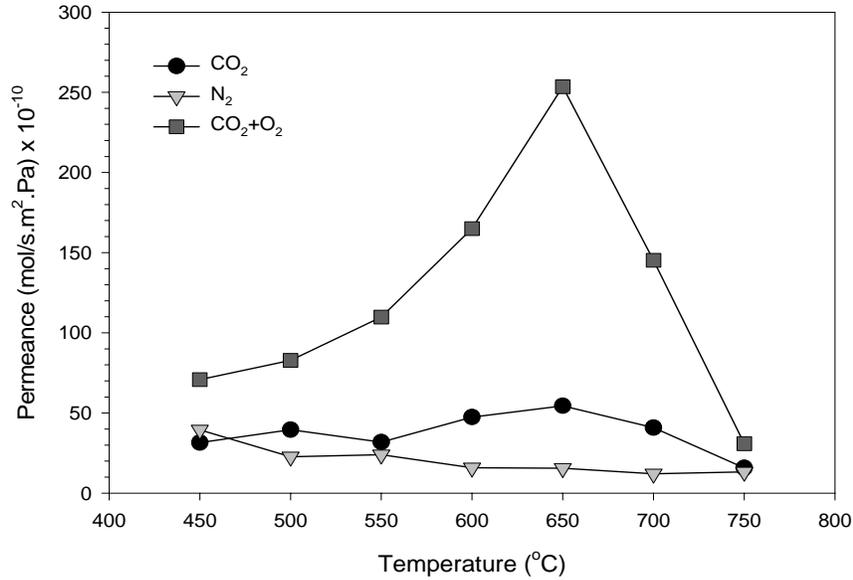
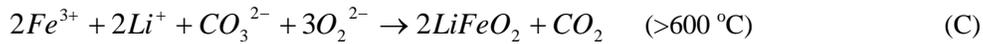
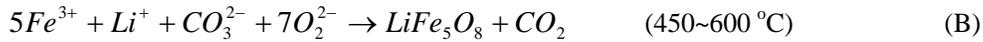


Figure 2 Gas permeance for pure CO₂, N₂, and the CO₂/O₂ mixture at different temperatures

Pure CO₂ and N₂ are unlikely to ionize, hence the limited transport that is observed through the molten carbonate phase. On the other hand, the results confirmed the idea that CO₂ and O₂ ionize to form CO₃²⁻. However, after 650°C, the increase in temperature was a detriment to the transport of CO₂/O₂. Eventually, the temperature increase caused permeance to decrease to just above that of which was observed for the pure gas measurements for CO₂ and N₂.

Potential causes for the decrease in permeance CO₂ at temperatures above 650°C were sought to provide insight to the problem. Membranes used during high temperature permeation tests were examined using XRD. The XRD results indicated that LiFe₅O₈ and LiFeO₂ were present on the surface of the support. A literature search of this problem led to the realization that, in the presence of oxygen and CO₂, molten carbonates will react with iron in the stainless steel supports to form lithium iron oxides [4].



LiFeO₂, in particular, has a very low conductivity (3x10⁻³ S/cm) [1]. Formation of this compound on the surface limits the transport of electrons to the upstream side of the membrane. Therefore, Reaction A becomes inhibited and formation CO₃²⁻ decreases. Consequently, the transport of CO₂ through the membrane is governed by a decrease in conductivity at high temperatures due to the formation of these lithium iron oxides [2,3].

To improve the high temperature stability of the dual phase membrane, a ceramic-like perovskite material has been proposed for use as the support material. Lanthanum-strontium-cobalt-iron (LSCF) material has been shown to have good electronic conductivity and should be able to

withstand the harsh conditions that the supports experience during high temperature permeation. Therefore, the possibility exists that the LSCF material can be used as a support for the dual phase membrane. During the past couple of months since our laboratory was moved from University of Cincinnati to Arizona State University, research in this project has been focused on the synthesis and characterization of these LSCF supports and LSCF-carbonate dual phase membranes. The remainder of this report will detail the synthesis and characterization of such.

EXPERIMENTAL

LSCF powder was prepared via the citrate method. Nitrate metal precursors and citric acid were placed in a 1500 mL beaker in the following quantities:

Table 1 Constituents of $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ Produced Via the Citrate Method

Material	Weight (g)
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	12.99
$\text{Sr}(\text{NO}_3)_2$	4.24
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	11.64
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	4.040
Citric Acid	38.52

The quantities above produce a 6:4 and 8:2 mole ratio of La:Sr and Co:Fe, which yields $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, a material for which there is sufficient data available in the literature for comparison sake. Approximately 150% excess citric acid is required to ensure a complete reaction of the metal precursors. Lastly, 1000mL of de-ionized water is added to the chemicals and placed on a hot plate.

For the first four hours, the covered mixture is heated and stirred at 105°C to allow for a complete polymerization reaction of the metal precursors and citric acid. Afterwards, the cover is removed and the temperature is raised slightly to 110°C to allow for vaporization of liquid. At the end of the process, a very thick, brick-red gel begins to develop. Constant monitoring of the process toward the end is necessary to prevent the gel from burning at the bottom of the beaker. Once the gel has begun to rise within the beaker, the material is removed from the hot plate and dried at 120°C in an oven for 24 hours. After drying, self-ignition of the organics is done at 400°C for two hours.

The remnants in the beaker are removed and ground in a mortar for 10 minutes to produce a fine powder. Preliminary sintering of the powder is done at 600°C and lasts for at least five hours. Once complete, the powder must be vigorously reground for at least 20 minutes to ensure that only very small particles remain. After grinding, the powder is used to make the supports for the membrane. Approximately 3.5 grams of powder is placed into a disk mold with a diameter of about 2.95cm. The mold is then placed into a Carver hydraulic press. For the first minute, the applied

load on the mold is maintained at 5000lbs. Afterwards, the load is increased to 20,000lbs and kept at that level for five minutes. Final sintering of the disks is done at 900°C for 24 hours, after which, the membranes are ready for use.

Unsteady state helium permeance of the LSCF membranes was tested at room temperature to verify that the material was porous. The average pore size of the supports was determined from steady state helium permeation tests [4]. Once pore size was known, infiltration of the LSCF supports with molten carbonate was evaluated. The molten carbonate phase consisted of a mixture of lithium (Li), sodium (Na) and potassium (K) carbonate on a molar ratio of 42.5:31.5:25. Ground powders of the carbonate mixture were placed into a crucible and heated past the melting point of the mixture (397°C) for infiltration in the supports. As was done with the metal supports, the LSFC supports were preheated for about 30 minutes at 550°C prior to infiltration of the molten carbonate. Once the support had been heated for the appropriate amount of time, the bottom surface of the support was brought into contact with the molten carbonate. It was not necessary to immerse the entire support, as capillary action caused molten carbonate to adequately fill the pores.

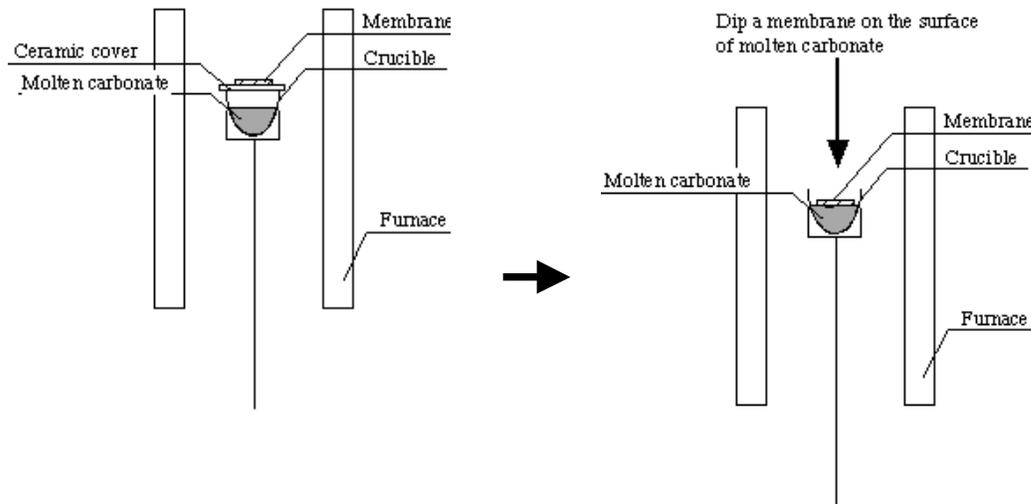


Figure 3 Preparation for Infiltration of Dual Phase Membrane with Molten Carbonate

The gas tightness of each membrane after infiltration was verified by performing unsteady state helium permeation tests at room temperature. During room temperature permeation tests, a rubber O-ring (West O-ring) was used to seal the membrane on both sides.

Finally, preliminary results used to determine the electrical conductivity were performed using the four-probe DC method. LSCF membranes were ground down to dimensions of 5mm by 18mm by 2 mm. Small notches were cut into the sides of the rectangle to relieve the stress on the edges of the membrane, thus decreasing the likelihood that the membrane would crack during preparation. Next, four lines of silver paint were painted around the rectangle, as shown.

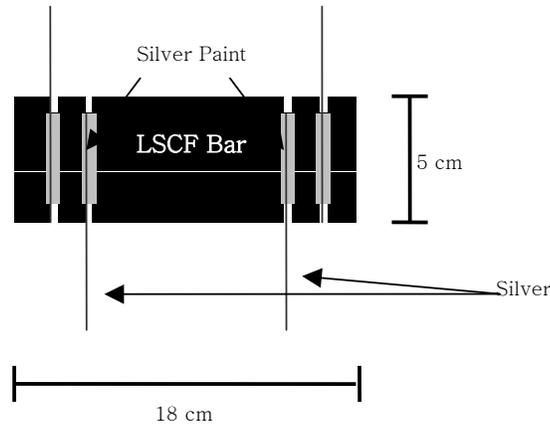


Figure 4 LSCF Preparation for Four-Probe DC Conductivity Measurements

After each wire is snug, paint is reapplied to maximize contact between the wires and the bar. The material was placed into the conductivity apparatus and heated to 900°C to soften the silver wire, allowing it to uniformly distribute on the surface of the material. Voltage and amperage data was taken at the desired temperatures to arrive at the conductivity of the sample.

RESULTS AND DISCUSSION

It is desired to create porous LSCF supports in order to take advantage of the capillary force that occurs during infiltration of the molten carbonate. Therefore, the first order of business was to determine whether the LSCF supports were porous. Unsteady state helium permeance was tested at various gauge pressures for two membranes from different batches of LSCF powder for comparison sake. Permeance for both membranes for the various gauge pressures is shown in Table 2.

Table 2 Unsteady State Helium Permeance of LSCF Membranes for Various Gauge Pressures

Gauge Pressure (psi)	LSCF 1 Permeance (moles/m ² ·Pa·s)	LSCF 2 Permeance (moles/m ² ·Pa·s)
5	4.26·10 ⁻⁶	7.58·10 ⁻⁶
10	5.39·10 ⁻⁶	7.96·10 ⁻⁶
15	5.62·10 ⁻⁶	8.32·10 ⁻⁶
20	5.73·10 ⁻⁶	8.60·10 ⁻⁶
25	5.88·10 ⁻⁶	8.87·10 ⁻⁶
30	6.10·10 ⁻⁶	9.07·10 ⁻⁶

Based on the fact that the permeance of the membranes was on the order of 10⁻⁶

moles/m²·Pa·s, the membranes were, in fact, porous. To determine the average pore size of the membranes, the steady state permeance method using helium was used. Creating a regression plot of permeance versus average pressure provides two constants, α and β often referred to as the Knudsen and viscous flow parameters. The slope and intercept of the regression lines are α and β respectively.

$$\alpha = 1.06 \left(\frac{\varepsilon}{\tau} \right) \frac{r_p}{L \sqrt{M_w RT}}$$

$$\beta = 0.125 \left(\frac{\varepsilon}{\tau} \right) \frac{r_p^2}{L \eta RT}$$

$$r_p = 8.48 \left(\frac{\beta}{\alpha} \right) \sqrt{\frac{\eta^2 RT}{M_w}}$$

Using the values of α and β made it possible to use the bottom equation to determine the average pore size (r_p), where η is the viscosity of the permeating species, T is the permeation temperature, R is the appropriate gas constant and M_w is the molecular weight of the permeating gas (*in this case, the permeating gas is He*). The pore sizes of LSCF 1 and 2 were found to be 0.37 and 0.57 μm respectively.

Preliminary tests have been conducted to determine the permeance of the membranes after infiltration of the carbonates. As was done for the metal support, the LSCF supports were infiltrated in a similar manner. A mixture of lithium (Li), sodium (Na) and potassium (K) carbonate on a molar ratio of 42.5:31.5:25 was placed into a vertical tube furnace and heated past the melting point of the mixture (397°C). LSCF supports were preheated inside the tube furnace above the molten carbonate mixture for approximately 30 minutes before infiltration. Preheating of the support is required to avoid the formation of a frosted carbonate layer. Supports that are not preheated and placed in contact with the molten carbonate mixture cause the carbonate to solidify rather quickly inside the pores of the material. Consequently, this inhibits the ability for molten carbonate to infiltrate the entire support. Preheating of the membrane avoids this problem altogether.

It was observed rather early in the process that the LSCF supports require a much longer dip coating time than the metal supports. The reason for this is that the pores of the metal supports were found to be about 7.8 μm , whereas the pores of the LSCF supports are more than 13 times smaller than that. Therefore, the carbonates are not likely to soak up as fast as was found for the metal supports. As a rough estimate, it appears to the supports require 10-15 minutes to completely fill with molten carbonates. On average, the supports increase by about 24.25% in weight after the dip coating process. Further research will be conducted on infiltration time and the effect that it has on the uptake of molten carbonate in these LSCF supports.

After some LSCF membranes were adequately filled with molten carbonate, their gas

tightness was tested to make sure the membranes were dense at room temperature. Permeance was, once again, determined via the unsteady state permeation method using helium as the permeating species. Recall that before infiltration, permeance of the LSCF membranes was on the order of 10^{-6} moles/m²Pas. Post infiltration, the permeance of the membranes decreased to 10^{-9} moles/m²Pas, indicating that the molten carbonate infiltrated the pores adequately. Permeance after infiltration of the metal membranes was on the order of 10^{-10} moles/m²Pas, so permeance of the LSCF membranes is one order of magnitude higher. Perhaps the fact that the LSCF support may have some pores that are too small to soak up the carbonate may lead to the absence of a completely infiltrated membrane. This could explain the slightly higher values for the permeance of He in comparison to the stainless steel support. Further research will be required to determine possible ways to optimize the dip coating process to see if lower permeance values can be achieved through different method.

Preliminary results for the electronic conductivity of LSCF at high temperatures are shown in Figure 5.

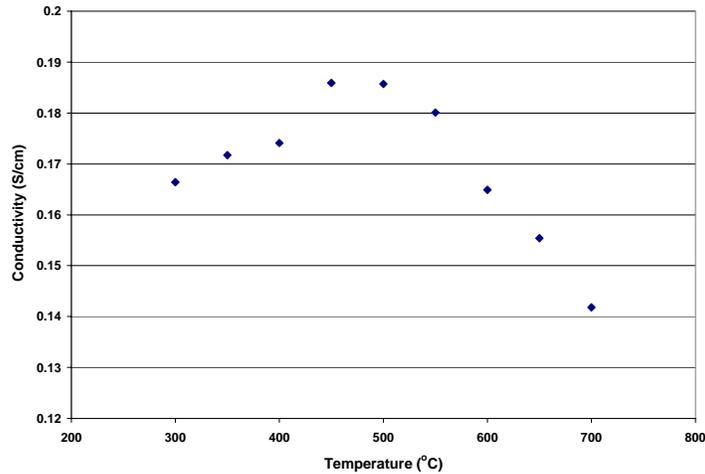


Figure 5 Conductivity of the LSCF Supports at Various Temperatures

The results of the conductivity experiments match trends reported by Qing Xu and co workers [5]. In the above graph, the conductivity of the LSCF material sintered at 900°C reaches a maximum at about 550°C. Results from the literature indicate that the maximum conductivity of LSCF material sintered between 1100 and 1250°C occurs at 600°C. However, while the same trend is observed between the data above and that in the literature, the magnitude of the values for conductivity is about four orders of magnitude lower. The difference between the two results could be due to the fact that the LSCF membranes prepared for this research are sintered at a relatively low temperature in comparison to the material used in the literature. The lower sintering temperature causes the material to be highly porous, and it is this increase in porosity that could lead to the low values of conductivity. Further studies may be performed to determine the effect of porosity on the

conductivity of these LSCF support.

CONCLUSIONS

Stainless steel supports are not stable during high temperature, dual phase membrane separation of CO₂ due to the formation of lithium iron oxides on the surface of the supports. Consequently, a new material has been sought to alleviate that very problem. It has been proposed that La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} is a suitable candidate for the support material in the dual phase membrane. Results published in the literature indicate that the LSCF membrane has a high enough conductivity such that it can provide enough electrons for the ionization reaction of CO₂ and O₂ to form CO₃²⁻.

The permeance of the LSCF membranes for this research were shown to have permeances on the order of 10⁻⁶ moles/m²·Pa·s, proving that the membranes are porous after sintering at 900°C. The average pore size based on steady state helium permeance measurements was found to be between 0.37 and 0.57 μm. After infiltration with molten carbonate, the room temperature, helium permeance of the LSCF membranes decreased by three orders of magnitude to 10⁻⁹ moles/m²·Pa·s. This number, however, is one order of magnitude larger than the room temperature permeance of the stainless steel supports after infiltration with molten carbonate. Optimization of dip coating with molten carbonate will be evaluated to determine if lower permeance values can be obtained with the LSCF membrane.

Finally, conductivity measurements were evaluated using the four-probe DC method. Conductivity of the LSCF material was found to be at a maximum of 0.1859 S/cm at 550°C. The trend observed for the conductivity of the material versus temperature was seen to match closely to what has been published in the literature, but the values are four orders of magnitude smaller than those reported. Lower conductivity was expected due to the higher porosity of the supports tested for this research, but further measurements are necessary to verify the preliminary results.

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