

Dual Phase Membrane for High temperature CO₂ Separation

Technical Progress Report

(Final)

09/30/02

06/30/07

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October, 2007

DE-FG26-00NT41555

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ABSTRACT

This project 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. Permeation tests for CO₂ and N₂ from 450-750°C showed very low permeances of those two gases through the dual-phase membrane, which was expected due to the lack of ionization of those two particular gases. Permeance of the CO₂ and O₂ mixture was much higher, indicating that the gases do form an ionic species, CO₃²⁻, enhancing transport through the membrane. However, at temperatures in excess of 650°C, the permeance of CO₃²⁻ decreased rapidly, while predictions showed that permeance should have continued to increase with temperature.

XRD data obtained from used membrane indicated that lithium iron oxides formed on the support surface. This lithium iron oxide layer has a very low conductivity, which drastically reduces the flow of electrons to the CO₂/O₂ gas mixture; thus limiting the formation of the ionic species required for transport through the membrane. These results indicated that the use of stainless steel supports in a high temperature oxidative environment can lead to decreased performance of the membranes. This revelation created the need for an oxidation resistant support, which could be gained by the use of a ceramic-type membrane.

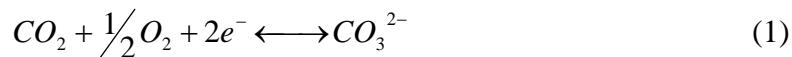
Work was extended to synthesize a new inorganic dual-phase carbonate membrane for high temperature CO₂ separation. Helium permeance of the support before and after infiltration of molten carbonate are on the order of 10⁻⁶ and 10⁻¹⁰ moles/m²·Pa·s respectively, indicating that the molten carbonate is able to sufficiently infiltrate the membrane. It was found that La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} (LSCF) was a suitable candidate for the support material. This support material proved to separate CO₂ when combined with O₂ at a flux of 0.194 ml/min·cm² at 850°C. It was also observed that, because LSCF is a mixed conductor (conductor of both electrons and oxygen ions), the support was able to provide its own oxygen to facilitate separation of CO₂. Without feeding O₂, the LSCF dual phase membrane produced a maximum CO₂ flux of 0.246 ml/min·cm² at 900°C.

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INTRODUCTION

Extensive research has been done in the past decade on microporous inorganic membrane for carbon dioxide (CO_2) separation. However, microporous inorganic membranes only give high CO_2 selectivity at low temperatures ($> 350^\circ\text{C}$). Therefore, dense inorganic membranes have been the focus of recent studies for high temperature CO_2 separation processes [1]. It is known that molten carbonate mixtures, 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 concept 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 consisted of a porous metal phase and a liquid carbonate phase, as shown in Figure 1. Metal supports were used because the material can supply electrons to facilitate the reaction that makes the concept of the dual-phase membrane possible. CO_2 and O_2 in the presence of an electron rich environment have the tendency to ionize and form CO_3^{2-} :



Separation can be accomplished with the driving force created by the CO_2 partial pressure gradient. On the upstream 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 CO_2 and O_2 can transport through the molten carbonate, the selectivity for CO_2 over N_2 or other gases is theoretically infinite.

We extended the dual-phase membrane concept to ceramic-carbonate membrane for improved oxidation resistance. Along this direction, we started prepared porous, electrically conductive, lanthanum cobaltite (LaCoO_3) perovskite supports for oxidative resistant ceramic-carbonate dual-phase membranes for high

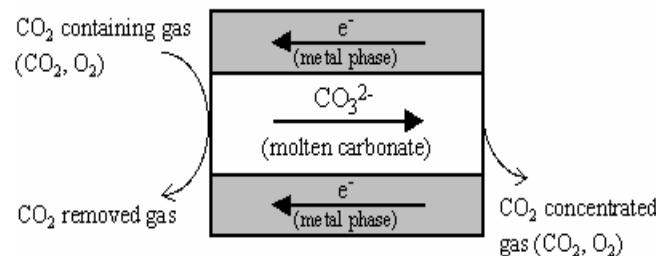
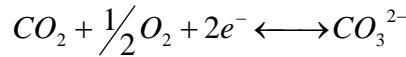


Figure 1: Membrane Wall Cross-Sectional View Illustrating the Concept of Dual Phase Metal-Carbonate Membrane for High Temperature CO_2 Separation

temperature separation of carbon dioxide.

EXECUTIVE SUMMARY

Dual-phase membranes for high temperature CO₂ separation were successfully prepared. Two different support materials were used; stainless steel and La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} (LSCF). Stainless steel supports were purchased commercially (Mott Corporation), while the LSCF supports were produced from powder made via the citrate method. The key factor in choosing both of these materials as the supports for the dual-phase membrane was their electronic conductivity, because the reaction that facilitates high temperature CO₂ separation using the dual-phase membrane requires a conductive support:

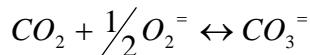


Beforehand, the helium permeance of the stainless steel and LSCF supports was on the order of 10⁻⁴ and 10⁻⁶ moles/m²·Pa·s respectively. The pore diameter, determined from steady state helium permeance measurements, was found to be approximately 400 nm for the stainless steel supports and 330 nm for the LSCF supports. Molten carbonate was infiltrated into the pores of both supports via the direct infiltration method. After infiltration, the helium permeance of both membranes was on the order of 10⁻¹⁰ moles/m²·Pa·s, indicating that molten carbonate successfully infiltrated the pores within the support.

High temperature permeation tests for the metal-carbonate dual-phase membrane were observed. CO₂ and N₂ permeance through the membrane from 450-750°C was low. This result was expected because, when fed alone, neither CO₂ nor N₂ should ionize. On the other hand, permeance of the CO₂ and O₂ mixture was higher, reaching a maximum permeance at 650°C. This showed that the gases (CO₂+O₂) do form CO₃²⁻, and that this particular species is mobile in the molten carbonate phase. As a result, separation was achieved. Yet, at temperatures above of 650°C, permeance through the membrane decreased. After high temperature experiments were completed, the surfaces of the membranes were examined by XRD. Data obtained from XRD analysis indicated that the surface of the membrane was covered with lithium iron oxides, causing separation to diminish because those particular compounds are insulators. As such, the flow of electrons to the surface was limited, limiting the formation CO₃²⁻.

It was the lack of oxidation resistance of the stainless steel support that fed the need for a support with higher oxidation resistance. Consequently, work was extended to determine the

separation characteristic of the LSCF dual-phase membrane. The material was found to be suitable for the support material of the dual phase membrane. At 850°C, the flux of CO₂ through the membrane with O₂ in the feed was 0.194 ml/min·cm². This value was slightly larger than the maximum flux observed for the stainless steel membrane at 650°C. It was also observed that, because LSCF is a mixed conductor, the support was able to provide its oxygen to facilitate separation of CO₂, as shown:



Without feeding O₂, the LSCF dual phase membrane produced a maximum CO₂ flux of 0.246 ml/min·cm² at 900°C. It is likely that CO₂ separation at high temperatures is governed by the diffusion of oxygen in the support. With this piece of knowledge, work on ceramic supports with higher value of oxygen ion conductivity is currently underway.

EXPERIMENTAL

Preparation of Metal-Carbonate Membrane

A mixture of 43.5/31.5/25 mol% of Li/Na/K 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 molten 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 had the smallest pore size (400 nm). Consequently, the molten carbonate could be stabilized in the pores due to 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 CO₃²⁻ 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.

Preparation of Ceramic-Carbonate Membrane

To prepare porous La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} (LSCF) supports, the parent powder was

prepared via the citrate method. Nitrate metal precursors from Fisher Scientific ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were weighted out in 6:4:8:2 molar ratios with 50% excess citric acid and approximately 1000 mL H_2O . After polymerization and condensation of the reactants, the remnants were dried in furnace at 110°C for 24 hours. Self-ignition of the organics was performed at 400°C in air for 2 hours. The resulting material was ground into a powder and placed into a crucible and calcined at 600°C for 24 hours. To form the supports, the LSCF powder was pressed into disk form. The resulting disk was sintered at 900°C for 24 hours. The porous LSCF supports were infiltrated with the molten carbonate of the same composition as the metallic dual-phase membranes. As with was the case with the metal supports, the direct infiltration method was used to prepare the dual-phase membrane. After allowing them to soak in the molten carbonate mixture for about 15-20 minutes, the supports were slowly lifted from the furnace and allowed to cool to room temperature. Excess molten carbonate was polished from the support surfaces.

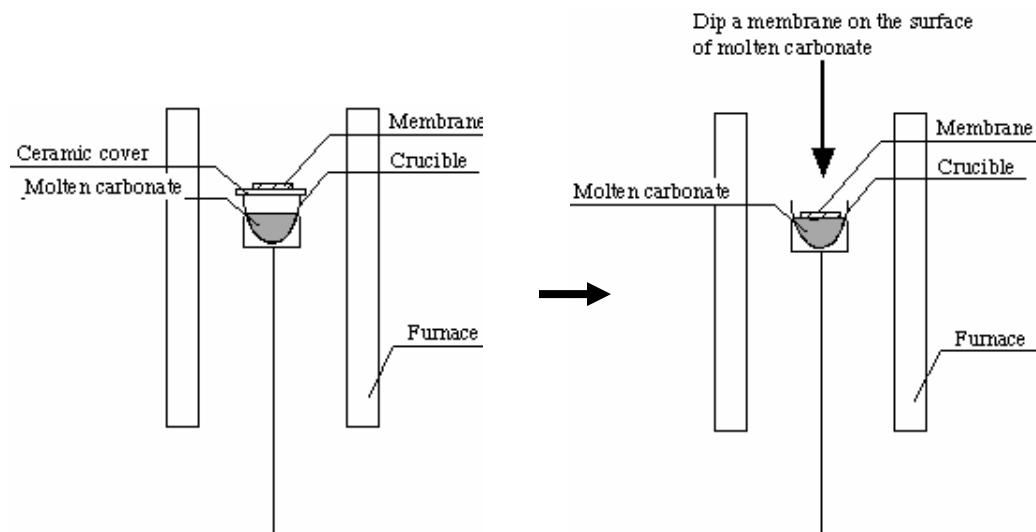


Figure 2: Schematic of Direct Infiltration Procedure for the Dual-Phase Membrane

Support and Dual-Phase Membrane Characterization

The pore-size and pore-size distribution of the uninfiltrated supports was measured by using steady state helium permeation and mercury porosimetry. Permeance, prior to and after infiltration, was determined from unsteady state helium permeation measurements. The phase structure and stability of the LSCF support material with molten carbonate was characterized by X-Ray diffraction (XRD) from 300-900°C (Bruker AXS, D8 Focus Diffractometer, $\text{CuK}\alpha$).

Electronic conductivity of uninfiltrated, sintered LSCF was measured by the four-point DC method. Conductivity measurements were obtained in a low oxygen partial pressure ($PO_2 = 10^{-4}$ atm), helium environment from 300-900°C. SEM imaging (Phillips XL-30) was performed to confirm the porous and dense nature of the supports before and after infiltration.

High Temperature Sealing of Metal Dual-Phase Membrane

Sealing membranes for experiments in 400-600°C under oxidizing atmosphere is a challenging problem. Various kinds of sealing materials were tested for the high temperature permeation cell. Conventional rubber o-rings were used to verify gas-tightness obtained during coating procedure because rubber showed best sealability at room temperature. Graphite displayed both good compressibility and temperature resistance, but could be oxidized with oxygen around the operating temperatures (450-500°C). Metal seals were also tested because it was easier to work with them.

Sealing of Ceramic Dual-Phase Membrane

High temperature permeation experiments for the ceramic dual-phase membrane performed by sealing the dual-phase membrane to a 1" OD alumina tube. The membrane could not be sealed in a compression cell due to the lower mechanical strength of the support in comparison to the metallic membrane. The LSCF dual-phase membrane was sealed to the tube by creating a paste composed of a mixture of LSCF powder (40 wt %), ground Pyrex™ beaker glass (50%), sodium aluminum oxide ($Al_2O_3\cdot Na_2O$; 10%) and water [2]. Paste was applied to the outside ring of the tube and the membrane was pressed firmly on top of the tube to form the seal. Additional paste was added to the outside edge of the tube and membrane interface to assure a gas-tight seal. After drying, the excess paste from the seal was polished off using Struers 800-grit SiC polishing paper.

The sealed tube and membrane were encased in a 1.5" OD alumina tube, which was sealed on both the feed and permeate side as to not let air seep in during experimentation. All gases used during heating and permeation are of industrial grade purity (99.9%). The system was heated at a rate of 1°C/min to 900°C. During heating, the feed side of the dual-phase membrane was allowed to heat in stagnant air, as to not starve the perovskite material of oxygen. 100 ml/min of CO_2 was fed to the membrane on the permeate/sweep side to limit decomposition of the carbonates. After allowing the system to remain at 900°C for one hour to allow the seal

set, the desired gases for high temperature permeation were initiated. Three hours was given before any data was collected to assure that the system had been given enough time to reach steady state.

RESULTS AND DISCUSSION

Metal-Carbonate Dual-Phase Membrane

The infiltration characteristics of the metal support and carbonate were examined. It was observed that if the support was at low temperature ($< 500^{\circ}\text{C}$) when it touched the surface of the molten carbonate, carbonates solidified on the surface of the support. This occurrence drastically limited infiltration of the molten carbonate into the pores of the support. On the other hand, when the support was at a high temperature ($> 500^{\circ}\text{C}$), there was no such formation of the ‘frozen carbonate layer’ and capillary action allowed for pore volume to be filled by the molten carbonate, which can be seen in Figure 3.

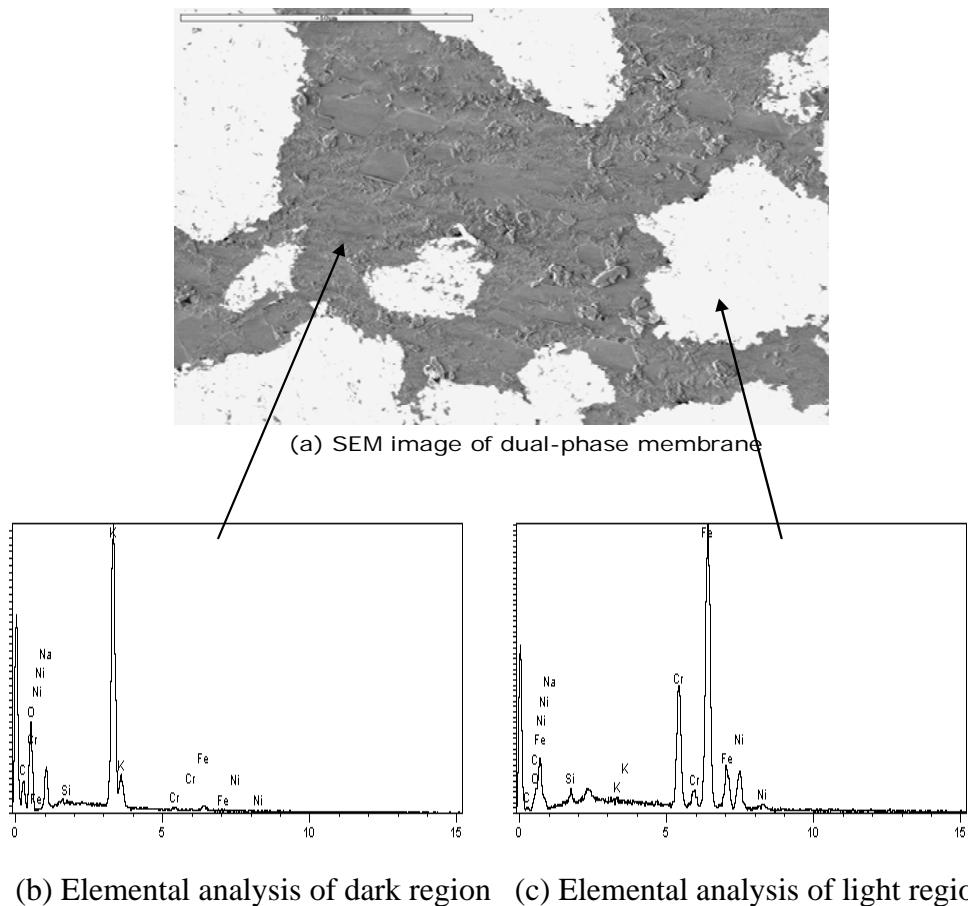


Figure 3: SEM/EDS Results of Metal Dual-Phase Membrane

Three different media grades (5, 2 and 0.5) of stainless steel disks were evaluated for use as the supports for the metal dual-phase membrane. One of the key features of these supports was the characteristic pore size. Infiltration of molten carbonate occurs in these pores because of capillary action. However, during high temperature permeation tests, the pressure gradient created between the up and downstream gases can be cause for concern. The force holding the molten carbonate in the pores has to exceed the pressure force; otherwise, “blowout” of the molten carbonate phase will occur, rendering the membrane ineffective. The radius of an individual pore that creates enough force to maintain the stability of the dual phase membrane was determined from the Laplace equation:

$$r = \frac{2\sigma \cos \theta}{P^1 - P^2} \quad (2)$$

The contact angle (θ) of the molten carbonate is considered to be zero due to the fact that in a high temperature, oxidative environmental, the molten carbonate phase is very wetable [3], hence the lack of any contact angle. The surface tension between the support and molten carbonate was determined from Equation 3 and the constants in Table 1.

$$\sigma = a - bT \quad (3)$$

Table 1: Constants Used in the Correlation for Surface Tension (Equation 3)

Temperature Range [K]	a [mN/m]	b [mN/m.K]	Correlated [mN/m] At 673K	Surface Tension At 773K
739-1062	287.1	0.0694	259.34	252.4

Using the calculated values for the surface tension, Equation 2 established that a minimum pore size of 9 μm was required to hold the molten carbonate in place. Table 2 shows the average pore size of the three kinds of supports considered for this research.

Table 2: Pore Size for Various Media Grade Supports

Media Grade	Average Pore Radius (μm)
5	83.6
2	73.5
0.5	7.8

Based on the calculations, only media grade 0.5 was applicable. This conclusion is further verified up by the fact that media grades 2 and 5 did not show sufficient gas tightness at room temperature (*helium permeance > 10⁻⁸ mols/s.Pa.m² at room temperature*) leading to the belief that molten carbonate did not completely fill or remain in the pores of those particular supports. Conversely, the dual phase membrane created from the 0.5 media grade showed helium permeance levels lower than 10⁻¹⁰ mols/s.Pa.m², showing the support has been sufficiently filled with molten carbonate.

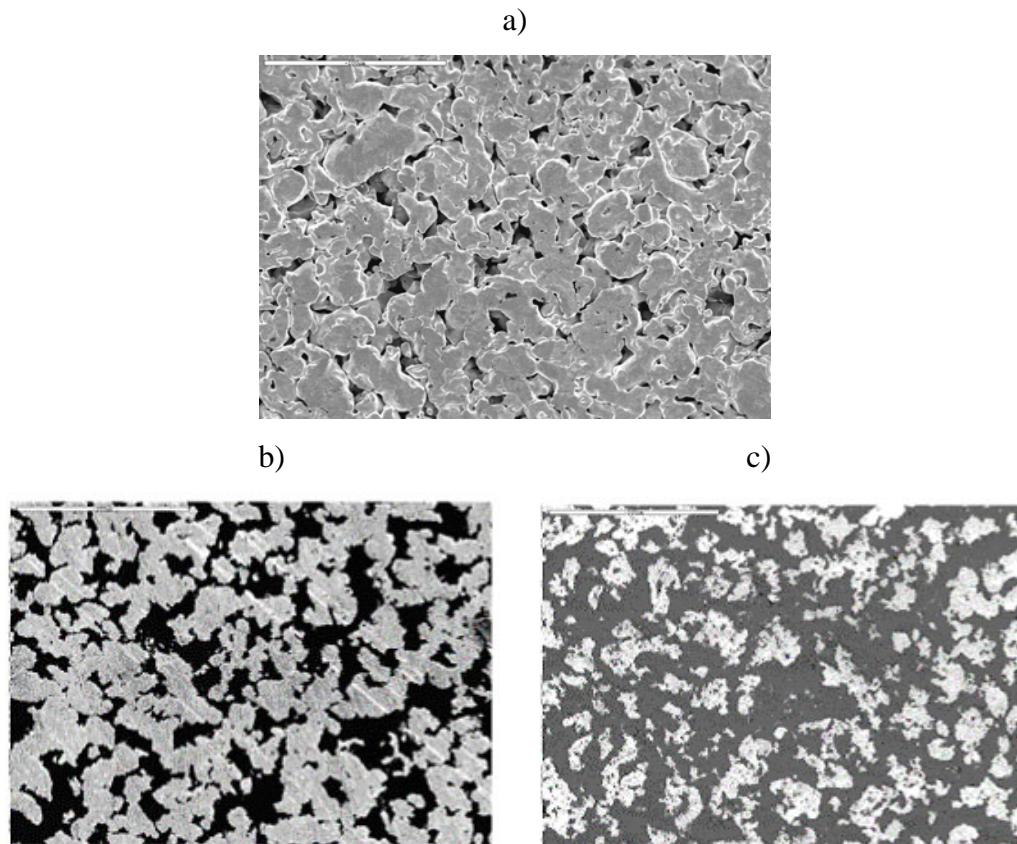


Figure 4: SEM Images of (a) Metal Support, (b) Molten Carbonate Contact Side of Dual-Phase Membrane, and (c) the Opposite Side of Dual-Phase Membrane

The theoretical maximum amount of carbonate that could infiltrate the support was determined to be 0.264 g. This value was based on porosity and density of the support. Using the following density correlation and the values in Table 3, the density of the support was calculated.

$$\rho = A - BT \quad (4)$$

Table 3: Constants Used in the Correlation for Density (Equation 4)

Melting Point [K]	A [kg/m ³]	B [kg/m ³ .K]	Correlated density [kg/m ³]	
			At 673K	At 773K
670	2512.8	0.5441	2295.16	2240.75

From the calculations, it was determined that 80% of the pore volume was filled by the molten carbonate after the dip coating process. This was visually confirmed from SEM imagines, which showed completely filled pores on both sides of the membrane.

The images given in Fig.4 confirm the notion that the molten carbonate infiltrates the support during the synthesis of the dual-phase membrane. The SEM images show that there are no empty pores within the support on either the contact or non-contact side. This proves that the capillary force is sufficient to fill the pores completely with molten carbonate. With the ability to sufficiently produce a dual phase membrane, the next step in the process was to perform CO₂ permeation experiments at high temperatures

The performance of the dual-phase membrane sealed with a gold gasket was examined over a temperature range of 450-650°C. Experiments were run for permeation of pure N₂, pure CO₂ and a CO₂/O₂ gas mixture. The results can be viewed in Figure 5.

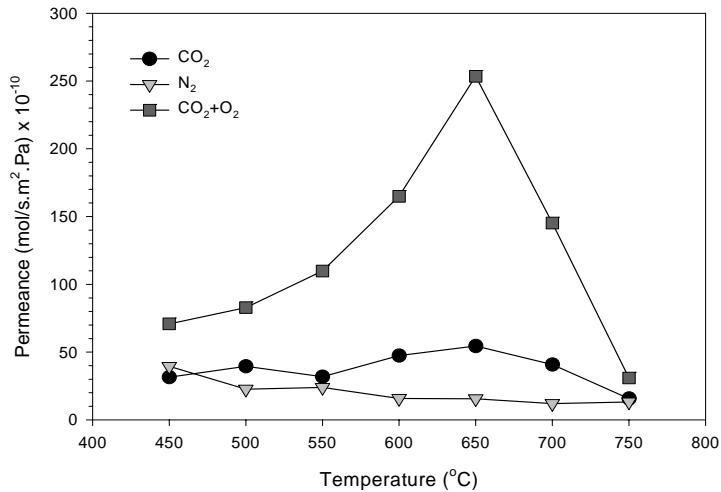


Figure 5: Gas Permeance for Pure CO₂, N₂, and CO₂/O₂ Mixture at Different Temperatures

The figure shows that the permeance of pure CO₂ and N₂ is very low to begin with, and

becomes even lower as the temperature is increased. The low permeance can be attributed to the fact that alone, CO₂ and N₂ are unlikely to ionize, hence their limited transport through the molten carbonate phase. Furthermore, the graph reaffirms the notion that the ionization of CO₂ and O₂ occurred. This is evident because the CO₂/O₂ mixture had the higher levels of permeance at every recorded temperature. 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 nearly that of which was seen for the pure gases.

The neutral flux of CO₂ through the dual phase membrane is related to the conductivities of the ionic species, CO₃²⁻, and the electrons (e⁻) in the metal support.

$$J_{CO_2} = -\frac{3RT}{8F^2L} \int_{P_t'}^{P_t''} \frac{\sigma_{ion}\sigma_{el}}{(\sigma_{ion} + \sigma_{el})} d \ln P_t \quad (5)$$

Since the conductivity of the electrons (σ_{el}) in the support (~ 10⁴ S/cm) is much more dominant than that of the conductivity of molten carbonate (σ_{ion} , 0.5-2.0 S/cm), the following simplification could be made:

$$\frac{\sigma_{ion}\sigma_{el}}{\sigma_{ion} + \sigma_{el}} \approx \frac{\sigma_{ion}\sigma_{el}}{\sigma_{el}} = \sigma_{ion} \quad (6)$$

With this simplification, integration of CO₂ produces Equation 7:

$$F_{CO_2} = \frac{9RT}{16F^2L} \sigma_{ion} \ln \left(\frac{P_t'}{P_t''} \right) \frac{\epsilon}{\tau} \left[\frac{1}{(P_t' - P_t'')} \right] \quad (7)$$

The conductivity of CO₃²⁻ (σ_{ion}) as a function of temperature was described empirically by Equation 8:

$$\sigma_{ion} = 83.8192 \exp\left(\frac{-3716.7}{T}\right) [S/cm] \quad (8)$$

From Equation 8, one could expect the ionic conductivity of the CO₃²⁻ species to increase as temperature rose, but as it was shown earlier, that is not the case. The actual results versus that of what was predicted by Equation 8 are shown in Figure 6. From 450 to 650°C, the data agrees reasonably well with the experimental results. Beyond 650°C, there is a huge discrepancy

between the predictions and actual results.

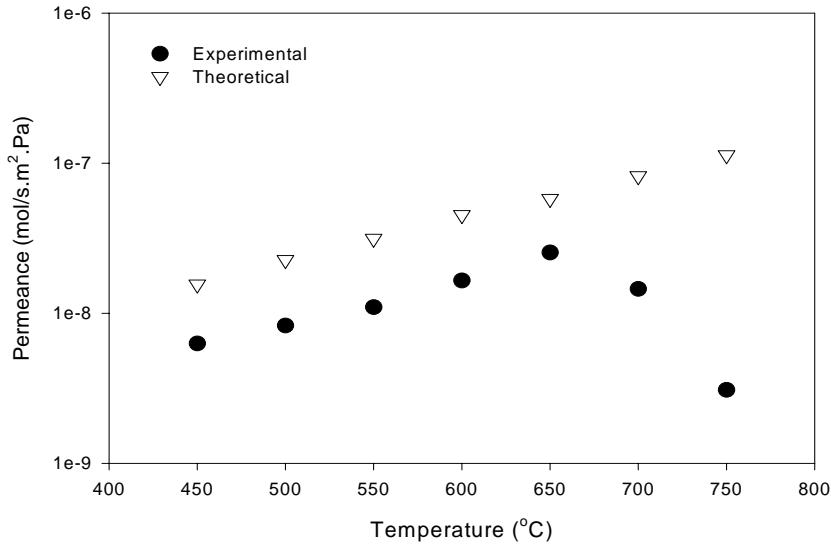
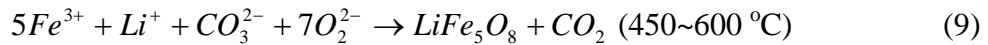


Figure 6: Comparison of Experimental and Theoretical CO_2 Permeance at High Temperatures

Potential reasons for the decrease in permeance of the membrane temperatures above 650°C were sought to provide insight to the problem. The stainless steel dual-phase membrane was examined post experimentation using XRD. The XRD results showed that LiFe_5O_8 and LiFeO_2 formed on the surface of the membrane during high temperature permeation tests. Previous research has indicates that, in the presence of oxygen and CO_2 , carbonates will react with the iron containing supports to form lithium iron oxides [4].



LiFeO_2 , in particular, has a very low conductivity ($3 \times 10^{-3} \text{ S/cm}$) [5]. Formation of this compound on the surface of the membrane limits the transport of electrons to the CO_2 and O_2 gas mixture on the upstream side of the membrane. Therefore, the reaction becomes inhibited and formation CO_3^{2-} decreases. Consequently, the transport of CO_2 through the membrane is governed by a decrease in conductivity at high temperatures due to the formation of these lithium iron oxides [5, 6].

Ceramic-Carbonate Membranes

Helium permeance for the LSCF supports was found to be on the order of 10^{-6} mol/m²·Pa·s. Steady state helium permeance and mercury porosity measurements were both used to determine the pore size of the LSCF supports. The result of the mercury porosimetry measurement for LSCF is given in Figure 7. Both methods indicated that the average pore radius of the LSCF support was approximately 330 nm.

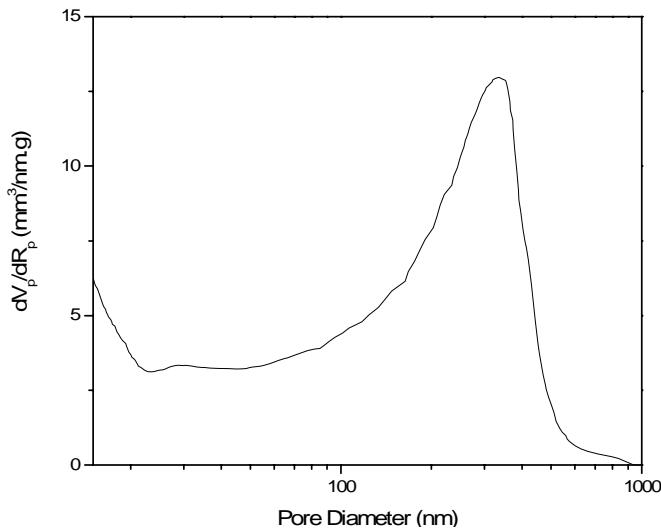


Figure 7: Mercury Porosimetry of LSCF Support for Pore Size Evaluation

Electronic conductivity of the LSCF supports was measured by the four-point DC method. Figure 8 shows conductivity of the support as a function of temperature. The trend shown in Fig 8 matches that of the trends reported by Xu et al. for the same material [7]. However, values reported in this work are about an order of magnitude less than those in their work. It is believed that the porosity, as a result of the lower sintering temperature, is the cause of the decrease in electronic conductivity. Nevertheless, the conductivity of the LSCF support is sufficiently high for use as the electron supplier for the dual-phase membrane.

The porous LSCF supports were infiltrated with the molten carbonate to obtain the dual-phase membrane. The permeance of the infiltrated membranes was on the order of 10^{-10} moles/m²·Pa·s. This indicates that the direct infiltration procedure is an acceptable method to produce dense dual phase membranes for this application.

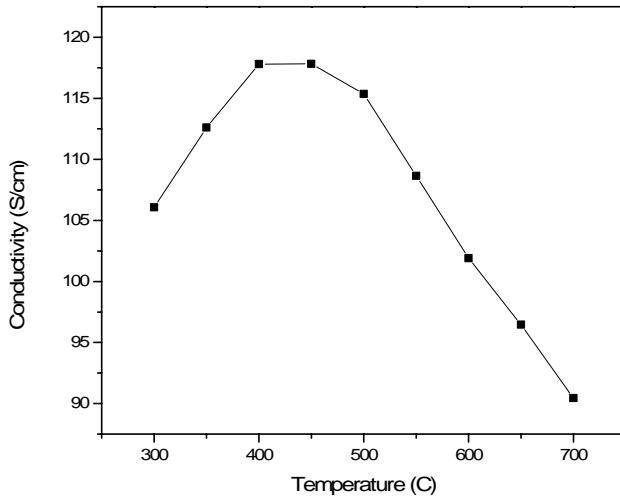


Figure 8: Electronic Conductivity of LSCF Support

Figure 9 shows the XRD results of the stability tests conducted on the 50/50 weight-percent mixture of LSCF and molten carbonate after heat-treatment in air at various temperatures for 48 hours. Peaks at 25.2° and 28.4° in the LSCF + Li/Na/K XRD scans represent the carbonate contributions. As can be seen, there is little change between the pure LSCF scan at room temperature and those done between 300-600°C, indicating the LSCF remains the major phase in 48 hours.

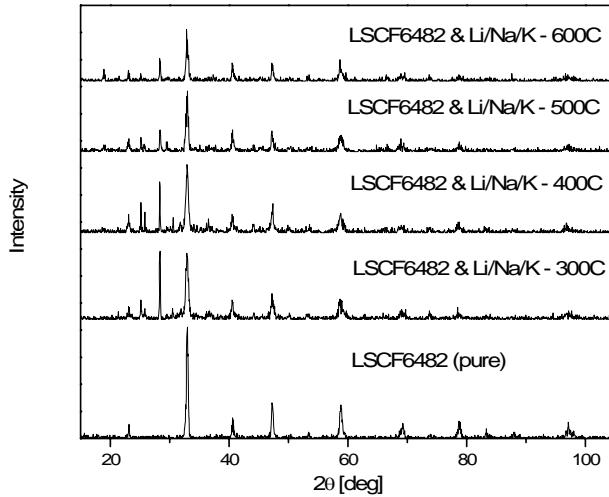


Figure 9: Stability of LSCF & Molten Carbonate as Determined by XRD Analysis

Two separate permeation experiments were conducted on infiltrated LSCF membranes of identical weights and thicknesses. Permeation was tested by feeding only Argon (Ar) and CO_2 at 50 ml/min each to the upstream membrane surface, and He (100 ml/min) as the sweep gas in the

downstream membrane surface. For both experiments, gas chromatograph (GC) readings showed no sign of Ar leaking into the permeate indicating both a perfect seal and infinite selectivity of CO₂/Ar. The LSCF-carbonate membrane has a remarkably high flux without feeding O₂, thus showing that the infiltrated membrane can, and does provide its own O₂⁼ to feed the reaction. At 900°C, the CO₂ flux was 0.246 ml/cm²·min. This value corresponds to a CO₂ permeance of 3.8·10⁻⁸ moles/m²·Pa·s.

CONCLUSIONS

Metal and ceramic-carbonate dual phase membranes were prepared via the direct infiltration method. Permeation tests for CO₂ and N₂ at 450-750°C show very low permeances of those two gases through the metallic dual-phase membrane, which was expected due to the lack of ionization of those two gases. Permeance of the CO₂ and O₂ mixture was much higher, indicating that the gases do form an ionic species, CO₃²⁻, enhancing transport through the membrane. However, at temperatures in excess of 650°C, the permeance of CO₃²⁻ decreased quite rapidly, while predictions showed that permeance should have continued to increase. The formation of insulating iron oxides on the surface rendered the membranes ineffective at higher temperatures. It was found that La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} was a suitable candidate for the support material of the dual-phase membrane. The material proved to separate CO₂ when combined with O₂ with a flux of 0.194 ml/min·cm² at 850°C. Perhaps the most interesting aspect of the work is that mixed conductors, such as LSCF, are able to provide oxygen to facilitate separation of CO₂. Without feeding O₂, the LSCF dual phase membrane produced a maximum flux of 0.246 ml/min·cm² at 900°C.

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