

Novel Ceramic Membrane for High Temperature
Carbon Dioxide Separation

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ABSTRACT

A new CO₂ semi-permeable dense inorganic membrane consisting of a porous metal phase and molten carbonate was proposed. A simple direct infiltration method was used to synthesize the metal-carbonate dual-phase membrane. Hermetic (gas-tight) dual phase membrane was successfully obtained. Permeation data showed that nitrogen or helium is not permeable through the membrane (only CO₂, with O₂ can permeate through the membrane based on transport mechanism).

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INTRODUCTION

The objective of this research is to develop inorganic membrane for carbon dioxide separation from flue (or coal gasification gas) in the temperature range of 350-550°C. In the first half year of Year II research, we focused on understanding the CO₂ sorption/desorption mechanism on lithium zirconate. Considering the all obtained data, we proposed a double layer model to describe the CO₂ sorption/desorption behavior of lithium zirconate. In the model, final product after CO₂ sorption is a particle which consist of ZrO₂ core inside and Li₂CO₃ layer. In the pure Li₂ZrO₃, the formation of solid Li₂CO₃ shell inhibits transport of CO₂, resulting in very slow carbonation rate. On the other hand, doping K₂CO₃/Li₂CO₃ in Li₂ZrO₃ helps transforming the solid carbonate film to the liquid one during the carbonation reaction. CO₂ diffusion in this liquid (molten) carbonate film is very fast, promoting CO₂ sorption rate considerably. These results show that Li₂ZrO₃ is potentially an excellent sorbent for separation of CO₂ at high temperature. However, pure and modified Li₂ZrO₃ is not a good material for the CO₂ semi-permeable membrane proposed originally. Nevertheless, the CO₂ sorption and microstructure results of the K₂CO₃/Li₂CO₃ doped Li₂ZrO₃ show that molten carbonate is highly CO₂ semi-permeable. With these results, we came up with an innovative concept of high temperature CO₂ permselective membrane using the molten carbonate material instead of lithium zirconate.

In the second half of YEAR II in Phase I research, we succeeded in preparing the hermetic (gas-tight) dense inorganic membrane consisting of a porous metal phase and molten carbonate. The metal phase not only provides the mechanical support but also is electronically conducting, reducing the overall mass transfer resistance for CO₂ permeation through the membrane. Permeation data showed that nitrogen or helium is not permeable through these membranes (only CO₂, with O₂ can permeate through the membrane based on the transport mechanism). Experimental results obtained so far in this research program show that the membrane offer promising properties for applications in membrane process for separation of CO₂ from flue (or coal gasification gas) at high temperatures (350-550°C).

CONCEPT-DUAL MEMBRANE FOR CO₂ SEPARATION-

Based on the results obtained so far, we proposed to prepare new CO₂ semi-permeable membrane using molten carbonate at high temperature. It is known that molten carbonate, such as Li₂CO₃/K₂CO₃ can conduct CO₃²⁻ at a very high rate. This is the basis of the molten carbonate fuel cell (MCFC). We proposed a dual phase metal-carbonate membrane for high temperature CO₂ separation. This membrane consists of a porous metal phase and a molten carbonate phase, as shown in Fig. 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 CO₂ partial pressure gradient. On the upper stream membrane surface CO₂, combining with electrons and oxygen, formed CO₃²⁻, which transports through the molten carbonate phase. The CO₃²⁻ releases electrons to form CO₂ and O₂ 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.

Based on the Wegner theory [1], the CO₂ permeation permeability for an electronic-ionic mixed conducting membrane is related to both ionic and electronic conductivities as:

$J_{\text{CO}_2} \propto [\sigma_e \sigma_i / (\sigma_e + \sigma_i)]$. With the presence of the metal phase the electronic conductivity becomes much larger than the ionic conductivity. Therefore, for the dual-phase metal-carbonate membrane the CO₂ permeation permeability is determined by the ionic conductivity only. If Li₂CO₃/K₂CO₃ with a CO₃²⁻ ionic conductivity in the range of 0.5-2 S/cm at 600°C and P_{CO₂} = 1 atm [2-4], the metal-Li₂CO₃/K₂CO₃ dual phase membrane would give CO₂ permeability of **2-10x10⁻¹⁰ mol/m.s.Pa** at 600°C. The CO₂ permeance would be **2-10x10⁻⁷ mol/m².s.Pa** for this new membrane of 1 mm in thickness, or larger if the membrane thickness is further reduced. Since only carbon dioxide (with oxygen) can transport through the molten carbonate, the selectivity for CO₂ over nitrogen or other gases is theoretically infinite.

EXPERIMENTAL

Synthesis of Dual-Phase Inorganic Membranes

We developed a simple direct infiltration method to prepare a dual-phase metal-carbonate membrane. We used 43.5/31.5/25 mole% Li/Na/K carbonate as the molten carbonate. Melting point of Li/Na/K carbonate is below 400°C and it has a higher CO₃²⁻ ionic conductivity than other carbonates [5]. With the lower melting point as compared to other carbonates, Li/Na/K carbonate membrane could be used at temperatures down to about 400°C. Porous 316L stainless steel discs (Series 1000, Media Grade 5, 2 and 0.5) from Mott Metallurgy were used as the membrane substrate. The metal membranes are made by compacting metal particles, and they have an average pore diameter of about 10, 4 and 1 μm, respectively and porosity of about 40%. In synthesis of the dual-phase membrane by the direct infiltration method, one surface of the metal membranes was brought in contact with molten carbonate kept at a temperature above its melting point.

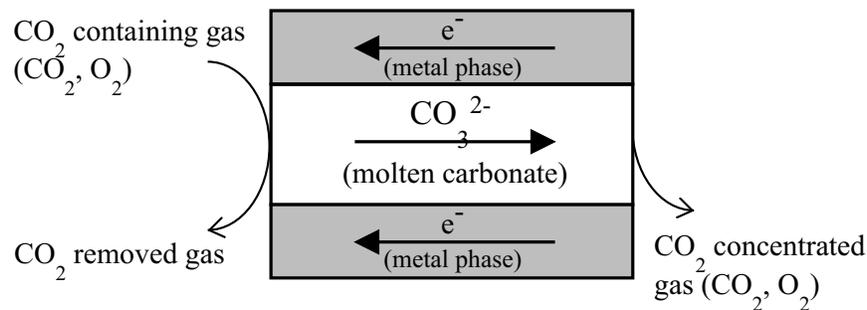


Figure 1 Membrane Wall Cross-Sectional View Illustrating the Concept of Dual Phase Metal Carbonate Membrane for High Temperature CO₂ Separation

Characterization

The dual-phase membrane, after quenched down to room temperature, was characterized by XRD for phase structure and He permeation for gas-tightness. The gas-tightness of the obtained dual phase membrane was examined using rubber O-ring as the seal by an unsteady state He permeation method at room temperature. High temperature stability of the molten carbonate in the porous metal supports and gas permeation properties of the dual-phase membranes were tested at 400-500°C on a gas permeation system with a graphite seal. The stability test was carried out by exposing the dual-phase membrane to a transmembrane pressure drop of about 1 atm and monitoring helium flow through the membrane. We also tried to test single gas permeation through the dual-phase membranes at high temperatures.

RESULTS AND DISCUSSIONS

In synthesis of the dual-phase membrane by the direct infiltration method, one surface of the metal membranes was brought in contact with molten carbonate kept at a temperature above its melting point. It was important to pre-heat the metal substrate in the same furnace as the carbonate. Otherwise, a thick dense carbonate layer could be formed on the surface of, not inside, the metal substrate. The first dip-coating experiment was carried out at 430°C, slightly higher than the carbonate's melting point. The result looked better than the case without pre-heating the metal substrate. However, there was still a thin carbonate film covering the surface of the metal substrate. Then, the temperature for the carbonate was raised to 500°C to reduce viscosity of the molten carbonate. Also the metal substrate was pre-heated for longer pre-heating time (15 min) at the same temperature. Good dual-phase metal-carbonate membrane was prepared under these conditions. Visual observation indicates that the pores of the metal membrane were completely filled with carbonate and there was essentially no carbonate layer covering the metal substrate membrane surface. XRD analysis clearly shows X-ray diffraction peaks of stainless steel and solid carbonate.

The results of the helium permeation tests show that a helium or nitrogen permeance is over 6 orders of magnitudes lower than the original porous metal substrates (helium permeance was reduced from 10^{-4} to 10^{-10} [mol/m².s.Pa]). This means that the obtained metal-carbonate membrane is very gas-tight and infiltration of metal membrane pore with the molten carbonate was very successful. Since helium or nitrogen will not permeate through the membrane and carbon dioxide will transport through the dense molten carbonate by the ionic transport mechanism, the gas-tightness would translate to a good permselectivity for carbon dioxide over helium or nitrogen for the dual-phase membrane at high temperatures.

High temperature stability tests show that the dual-phase membrane on Mott metal support of media grade 5 (pore diameter of about 10 μm), though hermetic to helium at the room temperature, lost its gas-tightness at 400°C during the stability test. It was found that the molten carbonate originally filled inside the metal pores was almost completely blown out from the pores at high temperature by the transmembrane pressure difference. The capillary force ($\Delta P = 2\sigma\cos\theta/r$, where σ is

surface tension and r is curvature) holds the molten carbonate within the membrane pore against the pressure difference. A rough calculation indicated that the pore diameter of the metal substrate should be smaller than $6\ \mu\text{m}$ in order to have the capillary pressure larger than 2 atm. We then prepared the dual-phase membrane on a Mott metal substrate with media grade 0.5 (pore diameter about $1\ \mu\text{m}$). This membrane remained hermetic to helium at 400°C and transmembrane pressure of 2 atm. The stability of the molten carbonate can be further improved by using the metal support with smaller pore size or pores with a more tortuous structure.

CONCLUSION

Based on the understanding of CO_2 sorption mechanism for lithium zirconate conducted in Year I and first half of Year II in the phase I project, we redirected our efforts to a new CO_2 permselective dense dual-phase inorganic membrane for separation of CO_2 from the flue gas in the temperature range of $350\text{-}550^\circ\text{C}$. In the year II so far, we succeeded in synthesizing the hermetic (gas-tight) metal-carbonate dual phase membrane. Permeation data showed that nitrogen or helium is not permeable through these membranes (only CO_2 , with O_2 can permeate through the membrane based on the transport mechanism). 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. It should be pointed out that this dual-phase membrane also permeates oxygen in an O_2/CO_2 molar ratio of 1:2. The warm $\text{CO}_2\text{-O}_2$ stream (2:1 ratio) separated from the flue gas by the membrane can find a number of applications.

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