

Dual phase membranes selectively transport CO₂ and are promising for potential applications in hydrogen production, natural gas separations, and energy conversion. These high temperature membranes consist of a molten carbonate (MC) salt supported in a porous, oxygen ion conducting ceramic[1]. Figure 1 shows two possible CO₂ transport mechanisms depending on whether the porous substrate containing the molten carbonate salt can transport oxygen anions (MOCC) or is electrically conductive (MECC). In the MOCC mechanism, at the feed side triple phase boundary (ceramic oxygen ion conductor, molten carbonate salt, gas phase), gas phase CO₂ reacts with oxygen anions (O²⁻) transported through the metal oxide oxygen conductor to form carbonate ions, CO₃²⁻, which must diffuse into the molten carbonate phase. If the porous substrate is electrically conducting (MECC), then CO₂ can react with an oxygen atom and an electron to form the diffusing carbonate ion. The molten carbonate phase typically consists of a mixture of carbonate salts[1]. The gas phase driving force is a partial pressure difference of CO₂, creating a concentration gradient in carbonate ions in the molten carbonate phase. When the carbonate ions arrive at the permeate side, the reverse reactions occur forming CO₂ as shown in Figures 1a and b. Using a mixed conducting LSCF ceramic support for the molten carbonate salt and a feed gas containing CO₂ and O₂, Lin and coworkers observed that CO₂ permeances (flux/driving force) were up to 11 times higher than for a feed gas with CO₂ alone (MOCC) at 800 °C [2]. Dual phase CO₂ transport membranes have the potential to be extremely selective for CO₂ over other gases such as N₂ or H₂ since these gases will have very low solubility in the molten carbonate salt.

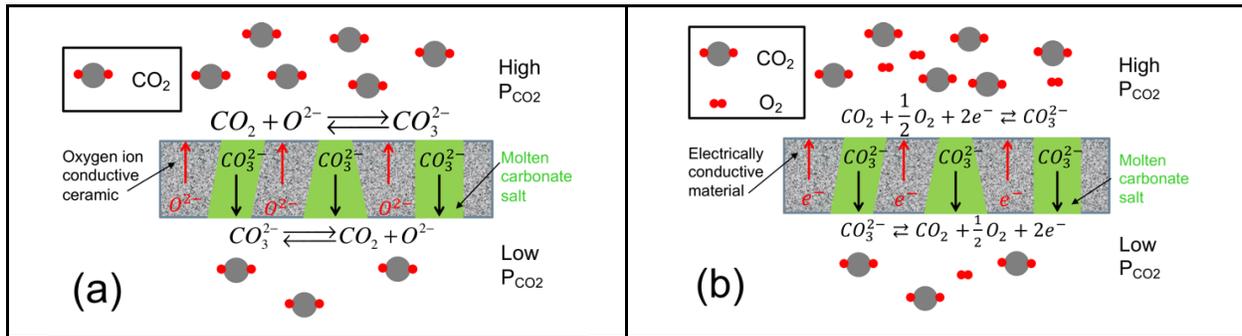


Figure 1. Cartoon illustrating the two possible CO₂ transport mechanisms in dual phase membranes. (a) mixed carbonate ion and oxygen ion conductor (MOCC); (b) mixed carbonate ion and electron conductor (MECC)

The proposed research has the general objective to investigate the influence of surface reaction rates/mechanisms on CO₂ transport in dual phase membranes supported in yttria stabilized zirconia (YSZ) porous substrates. We propose a new synthesis method for dual phase membranes to investigate the MECC transport mechanism. In order to make the substrates electrically conductive, the ceramic particles in the YSZ support were coated with a very thin layer of metal (Pd/Ag) using electroless plating to create electrically conductive pathways in the substrate. Adding the electrically conducting metal layer should enable both MOCC and MECC CO₂ transport mechanisms simultaneously. The metals were chosen for their resistance to corrosion by molten carbonate salts and their potential to catalyze the rate of carbonate ion formation[3, 4].

Nanoscale Ru crystallites were deposited on the 4YSZ substrate tubes obtained from Praxair Surface Technologies using wet impregnation followed by calcination and reduction in flowing H₂ to catalyze the heterogeneous Pd deposition on the substrate [5]. Electroless plating was then used to deposit thin sequential coatings of Pd followed by Ag on the previously activated tubular supports using previously published procedures[5, 6]. Due to the very short plating time, the metal plated YSZ tubes remained porous, but were now electrically conductive in the radial direction. Molten carbonate (MC) was incorporated into the metal coated YSZ tubes by dipping them into a molten eutectic Li/K carbonate mixture at 650 °C, and the dual phase membranes maintained their electrical conductivity after incorporation of the MC phase. As shown in Figure 2, the presence of O₂ in the feed gas stream increases the CO₂ permeance by over an order of magnitude at 720 °C compared to a feed gas containing only CO₂, as expected from the MECC transport mechanism. This is consistent with the data reported by Rui et al.[2] for dual phase LSCF ceramic (mixed conducting, both O²⁻ and electrons) membranes containing Li/K/Na molten carbonate salts. A maximum CO₂ permeance of over 10⁻⁷ mol/m².s.Pa was measured at 720 °C, very similar to the performance reported by Huang and coworkers[7].

The apparent activation energy for CO₂ transport calculated from the CO₂ permeance data in Figure 2 is 70 kJ/mol for the temperature range 450 to 650 °C (CO₂ + O₂ feed gas). The linear fit is excellent over this temperature range, but the CO₂ permeance values above 650 °C show significant positive deviations from the linear fit. This may suggest additional transport mechanisms for the higher temperatures, potentially related to the MOCC mechanism and oxygen anion conductivity. The apparent activation energy of 70 kJ/mol is significantly lower than the activation energy for oxygen ion transport of the 4YSZ substrate of 90 kJ/mol, suggesting that the MECC transport mechanism is occurring at 650 °C and below. In this temperature range the CO₂ permeance in our experimental system may be limited by the diffusion of carbonate ion in the molten carbonate phase.

Further evidence of carbonate ion diffusion as the rate limiting step is shown in Figure 3 where the CO₂ permeance at 650 °C is plotted versus the carbonate loading/thickness. As the mass of carbonate incorporated into the substrate decreases, the effective membrane thickness also decreases, and the CO₂ permeance increases in a linear fashion between 220 and 1100 μm thickness, also suggesting that carbonate ion diffusion is rate limiting. In their work with MECC dual phase membranes using porous Ag as supports for the LiK molten carbonate phase, Huang and coworkers reported that they observed surface reaction rate limitations below 840 μm[8]. It is possible that the presence of the platinum group metals Pd and Ru may catalyze some of the surface reactions shown in Figure 1b.

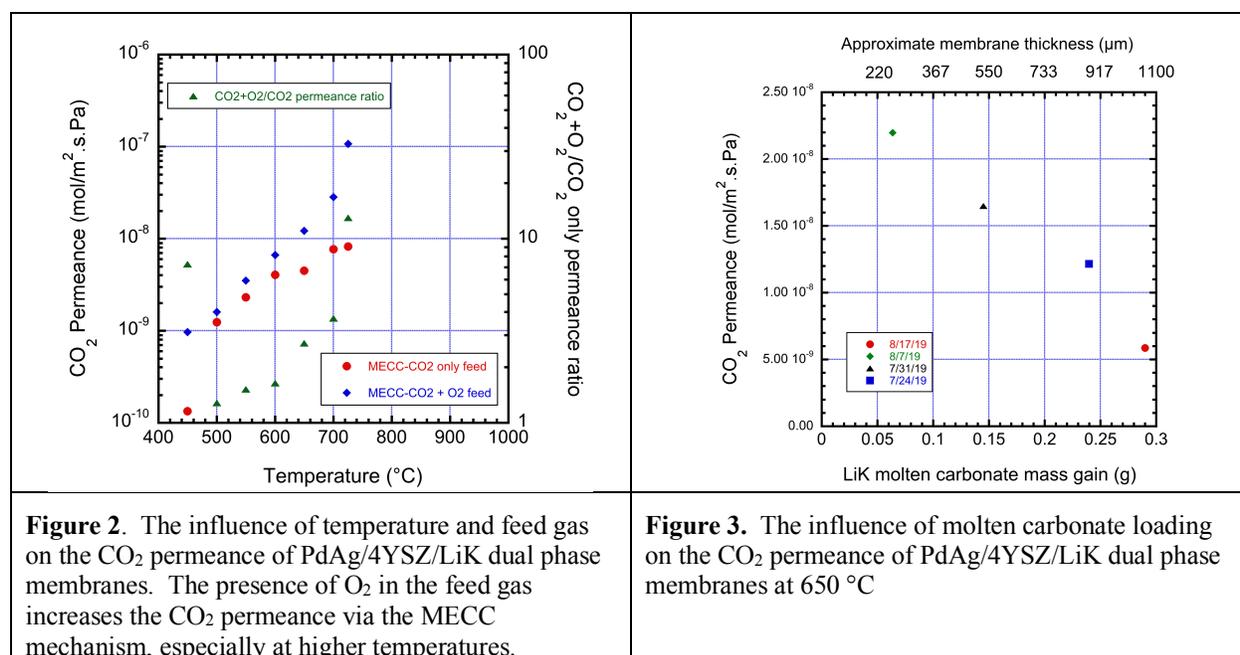


Figure 2. The influence of temperature and feed gas on the CO₂ permeance of PdAg/4YSZ/LiK dual phase membranes. The presence of O₂ in the feed gas increases the CO₂ permeance via the MECC mechanism, especially at higher temperatures.

Figure 3. The influence of molten carbonate loading on the CO₂ permeance of PdAg/4YSZ/LiK dual phase membranes at 650 °C

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Future work is to investigate Ni as the metal phase as it has been used extensively as a catalyst to increase the rate of CO₃²⁻ ion formation in molten carbonate fuel cells[9].

References

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