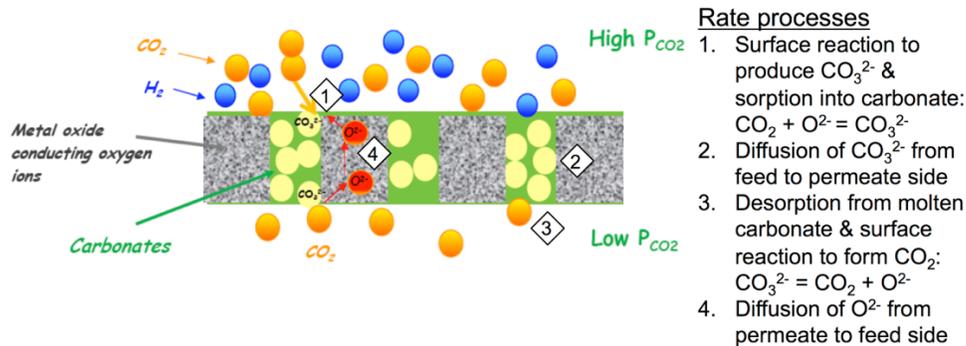


Dual phase membranes selectively transport CO<sub>2</sub> and are promising for potential applications in hydrogen production, natural gas separations, and energy conversion. These high temperature membranes consist of a molten carbonate (MC) salt supported in a porous, oxygen ion conducting ceramic<sup>1</sup>. As shown in Figure 1, at the feed side triple phase boundary (ceramic oxygen ion conductor, molten carbonate salt, gas phase), gas phase CO<sub>2</sub> reacts with oxygen anions (O<sup>2-</sup>) transported through the metal oxide oxygen conductor to form carbonate ions, CO<sub>3</sub><sup>2-</sup>, which must diffuse into the molten carbonate phase. The molten carbonate phase typically consists of a mixture of carbonate salts<sup>1</sup>. After these surface processes, carbonate ions diffuse from the feed side to the permeate side of the membrane. The gas phase driving force is a partial pressure difference of CO<sub>2</sub>, creating a concentration gradient in carbonate ions in the molten carbonate phase. When the carbonate ions arrive at the permeate side, having a lower CO<sub>2</sub> partial pressure, the carbonate ion desorbs from the molten carbonate and decomposes to CO<sub>2</sub> and an oxygen anion. The oxygen anion can then diffuse back from the permeate side of the membrane to the feed side through the ceramic phase. This transport mechanism has the potential to be extremely selective for CO<sub>2</sub> over other gases such as N<sub>2</sub> or H<sub>2</sub> since these gases will have very low solubility in the molten carbonate salt.



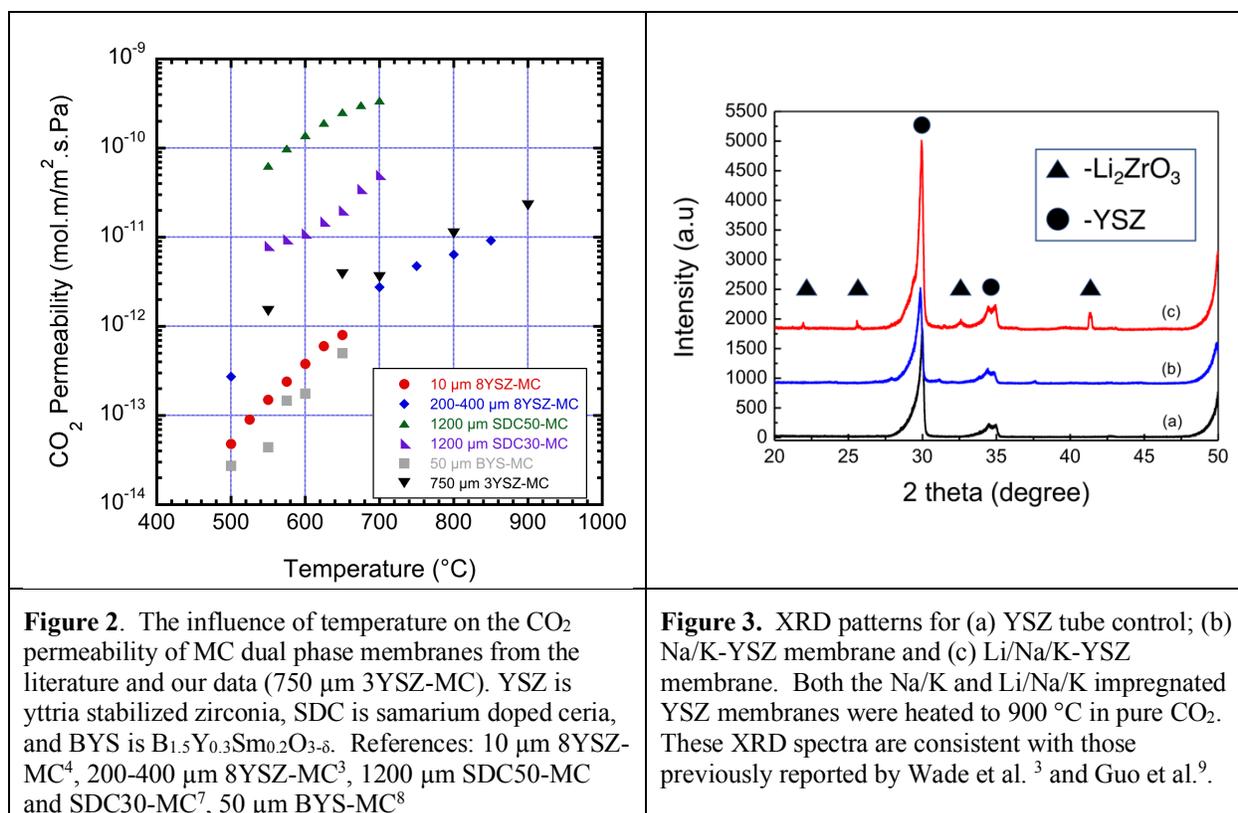
**Figure 1.** Cartoon illustrating the primary rate processes in dual phase membranes for high temperature CO<sub>2</sub> transport. Gas phase mass transport is neglected. The figure is adapted from Bredesen et al.<sup>2</sup>.

The proposed research has objectives to investigate whether metal catalysts can increase the surface reaction rate of CO<sub>2</sub> with O<sup>2-</sup> anions to form carbonate species and to investigate the effect of ceramic phase oxygen conductivity on flux and permeability by comparing similar, thin ( $\leq 20 \mu\text{m}$ ) dual phase membranes supported in 10Sc1CeSZ, 6Sc1CeSZ, and 3YSZ porous top layers with identical geometry with and without catalysts to increase the rate of surface processes.

Several experimental investigations of CO<sub>2</sub> transport in planar dual phase membranes from the literature, along with our recent data for a tubular membrane are summarized in Figure 2. Permeability is defined as the CO<sub>2</sub> flux normalized by the gradient in CO<sub>2</sub> partial pressure. The tubular membranes were prepared by impregnating a Na/K carbonate salt mixture into the pore structure of an asymmetric, 3YSZ filter manufactured by Praxair. The binary Na/K carbonate salt was used in our experiments because we observed the formation of a Li zirconate phase in XRD spectra (Fig. 3) after high temperature CO<sub>2</sub> transport experiments using a eutectic Li/Na/K carbonate mixture. Wade et al. observed that the CO<sub>2</sub> flux for a Li carbonate/YSZ membrane declined by four times over a 37 hour period and the membrane became very leaky<sup>3</sup>. They attributed this performance decline to the formation of a Li zirconate phase which was subsequently identified by XRD.

Our data, labelled “750  $\mu\text{m}$  3YSZ-MC”, compare very favorably to the literature, especially those from Prof. Wade and coworkers labelled as “200-400 8YSZ-MC”<sup>3</sup>. As expected, our CO<sub>2</sub> permeabilities are higher than much thinner membranes investigated by Prof. Lin and coworkers where surface reactions may become rate limiting<sup>4-5</sup>.

The apparent activation energy for CO<sub>2</sub> transport calculated from our data is  $107 \pm 13 \text{ kJ/mol}$ . This value is significantly higher than the activation energy for oxygen ion transport of the 3YSZ substrate of  $77 \text{ kJ/mol}$ <sup>6</sup>, suggesting that other rate processes besides diffusion of O<sup>2-</sup> may be rate limiting in our experimental system such as the surface reaction to form the carbonate ion (process #1 in Fig. 1).



A graduate student in chemical and biological engineering working on an MS degree was supported for an academic year by this grant.

Our experimental objectives for year 2 of this grant include: independent measurements of oxygen anion conductivity in our substrate materials (YSZ and ScCeSZ), reduction of the carbonate membrane thickness, and incorporation of catalyst materials to try to increase the rate of carbonate ion formation, and the CO<sub>2</sub> flux.

## References

- Chung, S. J.; Park, J. H.; Li, D.; Ida, J. I.; Kumakiri, I.; Lin, J. Y. S., Dual-Phase Metal-Carbonate Membrane for High-Temperature Carbon Dioxide Separation. *Industrial & Engineering Chemistry Research* **2005**, *44* (21), 7999-8006.
- Bredesen, R.; Xing, W.; Peters, T.; Fontaine, M.-L.; Evans, A.; Norby, T., CO<sub>2</sub> flux and separation properties of high temperature dual phase membranes, paper K2C. In *Int'l Conference on Inorganic Membranes (ICIM 13)*, Brisbane, Australia, 2014.
- Wade, J. L.; Lee, C.; West, A. C.; Lackner, K. S., Composite electrolyte membranes for high temperature CO<sub>2</sub> separation. *Journal of Membrane Science* **2011**, *369* (1-2), 20-29.
- Lu, B.; Lin, Y. S., Synthesis and characterization of thin ceramic-carbonate dual-phase membranes for carbon dioxide separation. *Journal of Membrane Science* **2013**, *444* (0), 402-411.
- Rui, Z.; Ji, H.; Lin, Y. S., Modeling and analysis of ceramic-carbonate dual-phase membrane reactor for carbon dioxide reforming with methane. *International Journal of Hydrogen Energy* **2011**, *36* (14), 8292-8300.
- Badwal, S. P. S., Zirconia-based solid electrolytes: microstructure, stability and ionic conductivity. *Solid State Ionics* **1992**, *52* (1-3), 23-32.
- Zhang, L.; Xu, N.; Li, X.; Wang, S.; Huang, K.; Harris, W. H.; Chiu, W. K. S., High CO<sub>2</sub> permeation flux enabled by highly interconnected three-dimensional ionic channels in selective CO<sub>2</sub> separation membranes. *Energy & Environmental Science* **2012**, *5* (8), 8310-8317.
- Rui, Z.; Anderson, M.; Li, Y.; Lin, Y. S., Ionic conducting ceramic and carbonate dual phase membranes for carbon dioxide separation. *Journal of Membrane Science* **2012**, *417-418* (0), 174-182.
- Guo, L.; Wang, X.; Zhong, C.; Li, L., Synthesis and CO<sub>2</sub> capture property of high aspect-ratio Li<sub>2</sub>ZrO<sub>3</sub> nanotubes arrays. *Applied Surface Science* **2011**, *257* (18), 8106-8109.