Nitrogen Selectivity of Molybdenum Metallic Membranes

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Nitrogen(N_2)-selective membranes are rare since nitrogen has low adsorption or dissolution affinity toward typical membrane materials. An efficient high-temperature N_2 separation using membranes would be beneficial if applied to post-combustion capture of CO_2 to increase the CO_2 concentration, or to the purification of natural gas, which contains N_2 as impurity. The ultimate goal of this study is to develop nitrogen-selective membranes that can be operated at high temperature.

A composite structure consisting of molybdenum (Mo) thin film on porous alumina was chosen as a model membrane system. Porous alumina substrates with pore sizes of approximately 100 nm were synthesized in the lab by colloidal casting and partial sintering. Subsequently, Mo membranes with thicknesses of 300 and 800 nm were deposited by physical vapor deposition techniques. Scanning electron microscope (SEM) images showed that the surface concentration of open pores along the triple boundaries decreased with the increase of thickness of the Mo layer. The electrical resistivities of the Mo layers were found to be 1.5×10^{-6} and 8.8×10^{-7} Ωm at 300 and 800 nm, respectively. The decreasing resistivity indicates that the structure becomes more dense, but the bulk resistivity of 5×10^{-8} Ωm was not yet attained. These results indicate that the membranes have defects but the thicker Mo membrane is more dense.

Gas permeation through the fabricated membranes was measured using pure N_2 and argon (Ar) to determine the ideal selectivity of the membranes at different temperature and pressure. The permeate pressure was maintained at 1 atm in the same gas as the feed in all experiments, and the reported pressure conditions in the following are Δp. The porous alumina showed an Ar permeance of 4.8×10^{-7} mol/(m^2·sec·Pa) at 22 ˚C and 4 bar. The permeance of Ar through the Mo membranes at the same operating conditions was significantly lowered to 38% and 0.9% of the support value after 300 and 800 nm deposition, respectively. For the 300 nm-thick membrane, a N_2 permeance of 1.0×10^{-7} mol/m^2·sec·Pa with an ideal permselectivity with respect to Ar of 1.4 was obtained at 800 ˚C and 4 bar. Because the open pores allowed Ar Knudsen diffusion, the selectivity was close to the Knudsen diffusion ratio of

N_2 to Ar (1.2), but the slight increment in selectivity indeed confirmed a solution-diffusion mechanism for N_2. For the 800 nm-thick membrane at 4 bar, the N_2 permeances were 6.5×10^{-10} and 7.2×10^{-10} mol/(m^2·sec·Pa), with the ideal permselectivities of 2.1 and 2.0 at 400 ˚C and 500 ˚C, respectively. Lower selectivity values of 2.0 (at 400 ˚C) and 1.8 (at 500 ˚C) were obtained at a higher Δp of 5 bar. The N_2 permeance, after the subtraction of the Knudsen diffusion permeance, showed a dependence on $p_{feed}^{0.5}-p_{permeate}^{0.5}$, which supports the hypothesis that transport of atomic nitrogen through the bulk Mo is possible.

The permeances of both Ar and N_2 at high temperature conditions were significantly lowered compared to what is expected from the temperature dependence of the Knudsen diffusion. This implies that defect pore sizes might have decreased at high temperature, possibly due to surface oxidation. Post-permeation analyses using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) revealed that the metallic Mo phase is still present after permeation tests, but also molybdenum oxide was formed. Nevertheless, the Mo membrane was stable for more than 90 hours at 400 ˚C with a trace amount of oxygen present in the flow system. After exposure to 600 ˚C, the Mo membrane appeared to have pinholes, observed by SEM. This is in agreement with the observation that no special selectivity persisted at 600˚C due to substantial membrane degradation.

The results in this study suggest that Mo metal can be used for N_2-selective membranes at moderately high temperatures. The formation of some surface oxide may help in reducing the size of pinhole defects although heavy oxidation leads to destruction of membranes. In future studies, the selectivity may be increased by improved metal membrane layers with a more dense microstructure.