High Permeation Condensation Membranes for Gas Separations

The separation of gasses is of importance in a wide variety of industrial processes. For example, the isolation of high quality hydrogen gas by separation from mixed gas streams is important for the commercialization of hydrogen fuel cells. Furthermore, cost efficient separation and removal of carbon dioxide from waste gas streams, such as those produced by electric power plants, could represent a large step forward in the reduction of greenhouse gas emissions. In this work, we are collaborating with Custom Materials, Inc. for the production, characterization, and testing of cellulose derived composite ceramic membranes for gas separation.

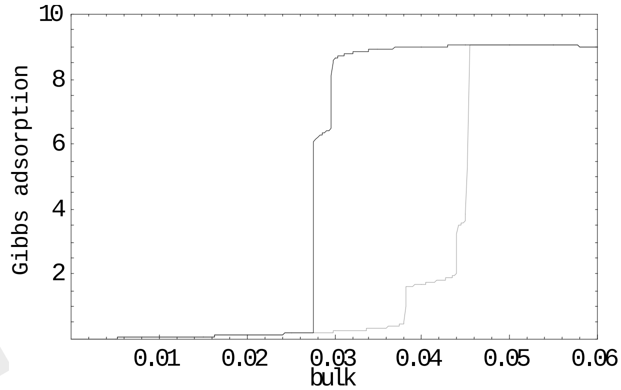
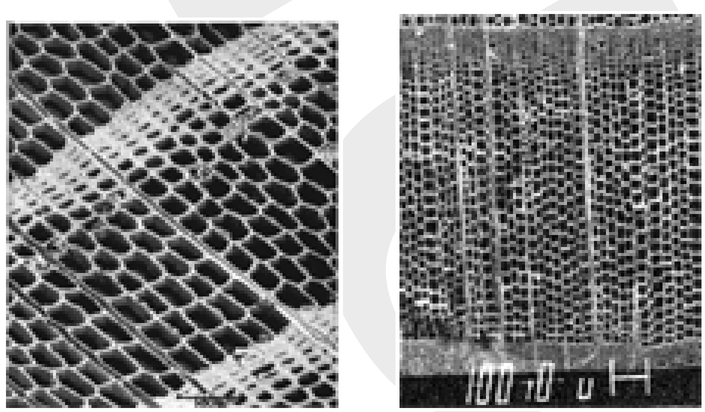


Figure 1: An example of a hysteresis curve in a porous material. The light branch is the adsorption branch, while the dark branch is the desorption branch. In this graph, the bulk density is proportional to the pressure of the gas.

These novel membranes work on the principle of capillary condensation[1,2], which is a separation based on differences in vapor pressures. In this process, the pore size distribution of the membrane must be very uniform, and the average pore size is larger in diameter than the largest component of the gas mixture to be separated. Separations achieved by this process allow for the isolation of a nearly pure stream of gas from a mixture, while the relatively large pore sizes allow for much higher fluxes than are possible with molecular sieves.



(a) before carbonization (b) after carbonization

Figure 2: Scanning electron micrographs of redwood.

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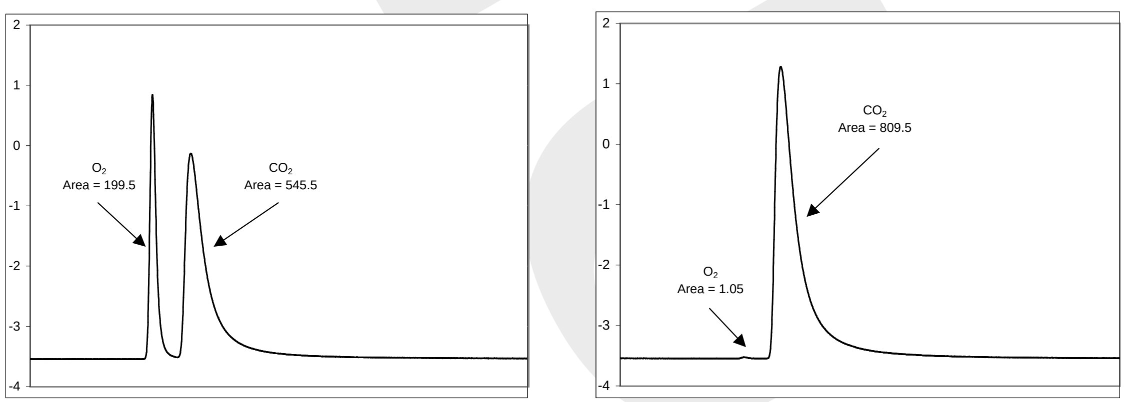
Capillary condensation is a well studied phenomena[3], which is illustrated schematically in Figure 1. Consider first the behavior of the most condensable component in the gas stream. Initially, when the pressure is low, it can be seen that the pore fills slowly with the gas. As the pressure rises, adsorption continues (following the bottom branch of the hysteresis curve in Figure 1) until a critical pressure is reached, after which the gas condenses inside the pore to form a dense, liquid like state. At this point, the pore becomes filled with liquid. This is the key to the separation process; an analogy would be a bathroom in which the ventilation is built into the shower drain. The vent will have no problem removing air from the room unless the shower is in use; however, when the drain is full of water, the water prevents the flow of air. In very crude terms, this is how the membranes work. Once condensation of the most condensable component is achieved, the pressure can be reduced while maintaining the pore filling. This can be seen by following the top branch of the hysteresis curve, as shown in Figure 1.

The challenge of this project is the construction and characterization of sufficiently robust membranes with which separation by capillary condensation is possible. In order to obtain membranes with a uniform distribution of pore sizes, cellulose and cellulose derivatives are being tested[4]. The two main options are wood, which has a highly connected pore structure and highly aligned fibers which give directional properties, and pulp, sawdust, filter paper, or other derived products, which have a more random orientation of fibers and uniform physical properties. These cellulose materials then are carbonized by thermal treatment in an inert environment at 1000^o C for 1 hour. Once treated, the membranes are converted to silicon carbide by liquid metal infiltration. Membranes made in this way are cost effective and can stand up to very high temperatures and pressures demanded of them in an industrial setting. An example of the microstructure of these membranes both before and after processing is presented in Figure 2.

Preliminary experiments using a Varian 3700 gas chromatograph equipped with a differential thermal conductivity detector show that it is possible to use the membranes made as



(a) feedstream composition

(b) post membrane composition

Figure 3: Separation of carbon dioxide from oxygen using a modified masonite membrane. The figures represent the separation before and after condensation in the membrane, respectively.

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described above for the separation of gasses. An example of the separation of carbon dioxide from oxygen is shown in Figure 3. The feedstream was composed of 30% oxygen and 70% carbon dioxide, as seen in Figure 3(a). The membrane is tested by slowly increasing the pressure on the feed side of the membrane. As the total pressure on the system increased to 210 psi, separation occurred and resulted in the post membrane composition depicted in Figure 3(b). The post membrane composition was 99% carbon dioxide, nearly completely excluding the less condensable component, oxygen. Separation continued as the total system pressure was lowered, with quantifiable separation occurring as low as 140 psi.

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