A Comparison of the Mass Transfer Performance of Conventional and Micromanufactured Porous Membranes

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ABSTRACT

Recent findings have suggested that the performance of absorption/desorption cycle micro-scale heat pumps can be significantly enhanced by the use of thin film gas/liquid contactors. In this study, it was hypothesized that microfabricated straight-through pores could significantly reduce the pressure drop for gas diffusion across a contactor as compared to the complicated and tortuous flow paths encountered in commercially available membranes. Below a comparison is made between the mass transfer performance of conventional membranes with those having engineered pores in an attempt to classify the mass flux characteristics of contactor membranes by the membrane morphology. Results show that the mass flux properties of woven membranes far exceed those of even engineered membranes.

Keywords: membranes, tortuosity, mass flux characteristics, contactors, absorption, desorption, heat pumps

INTRODUCTION

Microtechnology-based Energy and Chemical Systems (MECS) are massively-parallel microsystems fabricated in engineering materials capable of processing bulk amounts of fluid in microchannels.[1,2] MECS technology enables process intensification (i.e. the shrinking of energy and chemical process footprints) in an effort to distribute, decentralize and make portable energy and chemical systems such as heat pumps, chemical plants, and cytosensors. The miniaturization of MECS devices is made possible by the manifold improvement in the heat and mass transfer performance of systems due to the high surface area-to-volume ratios of the microchannel arrays within the devices.

Recent findings have suggested that the performance of absorption/desorption cycle micro-scale heat pumps can be significantly enhanced by the use of thin film gas/liquid contactors. However, a key limiting factor in the use of thin film gas/liquid contactors is the driving force across the contactor membrane with for the heat pump systems of interest is quite low (a few psi). Therefore, there is currently a great interest in understanding the nature of mass flux characteristics across contactor membranes. One hypothesis in this work was that a contactor membrane microfabricated with straight-through pores could significantly reduce the pressure drop for gas diffusion across a contactor as compared to the complicated, tortuous flow paths encountered in commercially available membranes. Below, two approaches to membrane fabrication are explored along with a comparison between the mass transfer performance of conventional and engineered membranes. The morphology of each membrane was studied by micrograph and related to the tortuosity factor calculated from mass flux measurements. The two engineered membranes are fabricated using laser micromaching and micromolding. The final outcome is an attempt to classify the mass flux characteristics of contactor membranes by membrane morphology.

EXPERIMENTAL APPROACH

A baseline for mass flux measurements was established by testing twenty-three different conventional membranes. To parse the enormous list of commercial membranes, some selection criteria were set that would most approximate the mass flux conditions for gas/liquid contacting. The selection criteria included that they be made from polymers with thicknesses between 50 and 150 μm and pore sizes from 1 to 10 μm.[1] Both had been tested and compared to the baseline of the mass flux measurements. No consideration was give up front for the chemical hydrophobicity (or hydrophilicity) of the membrane. In this study, only pressure drop measurements of membrane morphology were studied.

A test loop was developed capable of measuring the pressure drop across a membrane as a function of mass flux. The experimental setup for conducting the pressure drop testing across the conventional membranes involved flowing nitrogen from a tank through a needle valve (flow rate control) and into the lower plenum of a test fixture. Once in the test fixture, the nitrogen flowed across the membrane and into the upper plenum of the test fixture. The test fixture was necessary to ensure flow across a constant cross-section of each membrane. The diameter of the upper plenum was 2.0 inches while the lower plenum had a diameter of 0.4 inches. A stiffener was added to prevent the membranes from deflecting. The stiffener was 500 microns thick made from partially sintered stainless steel powder with a final pore size of 100 micron. An OMEGA HHP-2000 digital manometer was used to measure pressure drop between the upper and lower plenums. A

MKS Type M10MB (M10MB13CS3BV) mass flow meter was connected to the test loop at the output of the upper plenum. The test loop was designed to permit no more than 5% uncertainty in pressure drop (between 2 and 18 torr) and mass flux (between 200 and 1000 sccm).

Once a membrane was secured within the test fixture, the testing protocol involved first running the experiment up to the maximum recordable pressure drop or flow rate and then back down to zero. Between five and ten data points were collected in both directions.

MEMBRANE FABRICATION

Laser Micromachining Approach – A critical parameter for consistently producing 5-15 micron holes across the surface of the membrane is the depth of field (Z_R). The Gaussian beam expands rapidly beyond two times of the depth of field region. Assuming a 266 nm laser, a 0.5-inch focal length lens and an incident beam diameter of 1 mm, one half of the depth of field is found to be 53 micron. Therefore, theoretically, the total depth of field under laboratory conditions is only 106 µm. This is acceptable since the depth of the material used within this study was significantly less than 100 µm. Also, in order to consistently machine the material, a procedure was developed for consistently focusing the laser beam onto the workpiece surface. In addition, efforts were made to reduce the flatness of the workpiece material to within 100 µm.

Micromolded Approach – The PDMS membrane fabrication process can be divided into three major steps. The first step is to create SU8 posts on the substrate. Second step is to spin coat PDMS on to the substrate with SU8 posts in order to create PDMS membranes with straight through pores. The third step is to separate PDMS membrane from the SU8 mold and substrate. The permeability was evaluated from the test loop.

DATA NORMALIZATION

Conventional membranes tend to have tortuous flow paths and so it is expected that they will have a higher pressure drop than membranes with straight-through pores. However, other factors can affect the pressure drop across a membrane. For example, it is expected that thicker membranes will have higher pressure drops. In addition, membranes with higher pore packing density are expected to have lower pressure drops. In order to objectively analyze the pressure drop data collected, several equations were developed to help normalize the data.

The first consideration in normalizing the data is to consider the impact of open area or pore packing density. This parameter is easy to quantify for straight-through pores as it is the pore cross-sectional area times the number of pores per unit membrane area. For fibrous or other tortuous path pores, it is more difficult to quantify. In this thesis, open area or pore packing density is quantified by the fractional density of the membrane. The fractional density of the membrane is equal to the measured density of the membrane divided by the density of the membrane material.

The effect of the fractional density is to impact the total mass flux as follows:

$$\text{mass flux} = \frac{\text{mass flow}}{A_o} = \frac{\text{mass flow}}{(1-f)A} \tag{2}$$

where A_o is the actual open area through which the fluid flows, f is the fractional density of the membrane, and A is the nominal area of the membrane exposed to the fluid.

The effect of the membrane thickness is more straight forward. Assuming laminar flow conditions, pressure drop through a pore is assumed to be proportional to:

$$\Delta p \propto \frac{h \cdot V^2}{D_H} \tag{3}$$

where D_H is the hydraulic diameter and V is the average velocity through the channel. To compare membranes, we normalize pressure drop by dividing through by the membrane thickness, h:[3,4,5]

$$\frac{\Delta p}{h} \propto \frac{V^2}{D_H} \tag{4}$$

These two normalizing procedures are used to help identify patterns in the data and to draw conclusions about the effect of membrane morphology on the mass flux characteristics of the membrane.[5]

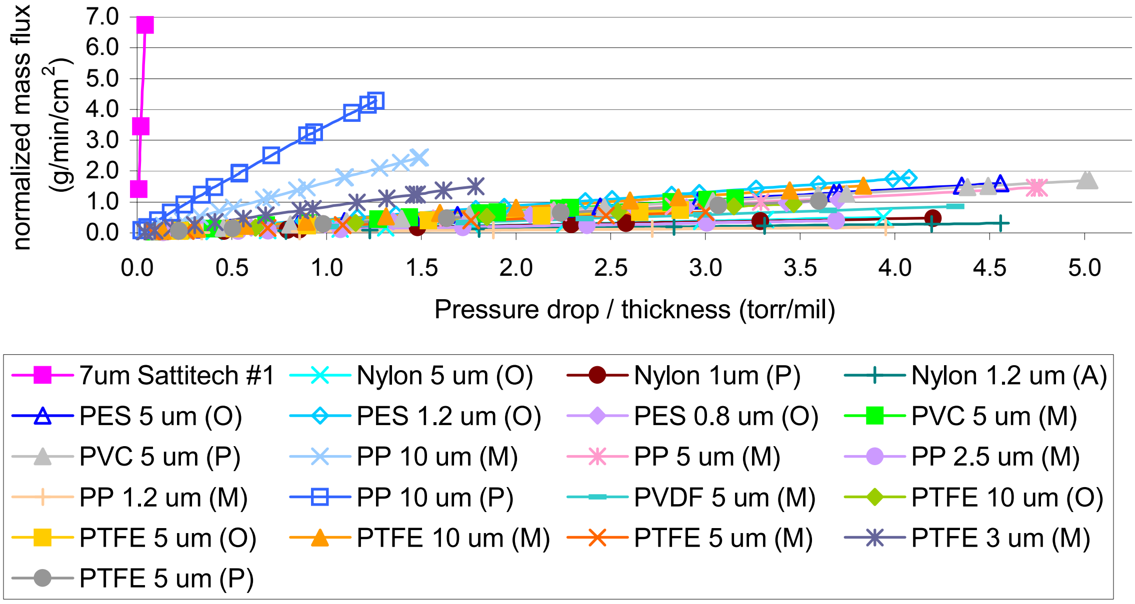


Figure 1. Normalized pressure drop results across the baseline membranes.

RESULTS AND DISCUSSION

Baseline Measurements – Figure 1, shows the normalized pressure drop results across each membrane using equations 2 through 4 above. An analysis of the morphology of these membranes showed that the membrane morphologies can be classified into three broad categories: woven, fibrous and networked. Networked membranes differ from fibrous membranes in that the membrane is an interconnected web of material while fibrous membranes are not connected with one another. One difference in these morphologies is that networked morphologies are sponge-like and may result in “dead ends” or flow terminations as the fluid winds through the structure. Fibrous morphologies are incapable of terminating flow paths. Therefore, it is plausible that the networked structures could provide higher pressure drops than fibrous structures.

Figure 2 shows the same normalized graph plotted for the three different morphologies investigated in the mass flux baseline. It supports the notion that in general, fibrous morphologies provide less pressure drop than networked morphologies. All of the better performing membranes are either woven or fibrous with woven membranes significantly outperforming the fibrous membranes.

Laser Micromachining Approach – A nominally 75 µm thick Kapton membrane was laser micromachined with an array of 22,500 straight-through holes (150 by 150 holes). The average pore size was found to be different on the front side than on the back side of the material due to the characteristic parabolic shape of the laser energy deposition. Using optical microscopy, the average pore size was found to be 16.5 ± 0.5 µm for the front side and 5.3 ± 0.8 for the back side at a 95% confidence interval (See Figure 3a and b).

In general, the mass flux results of the laser micromachined membrane did not show a significant

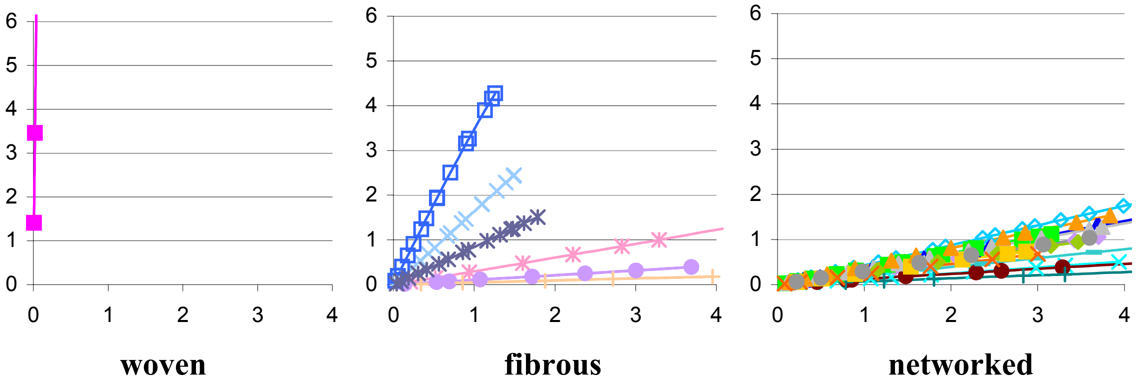


Figure 2. Normalized pressure drop results for (from left to right) woven, fibrous and networked structures

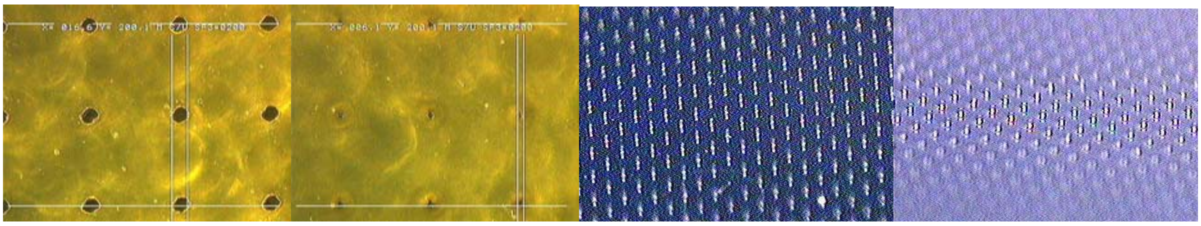
improvement over the commercial woven and fibrous membranes. In comparison to the networked membranes with similar pore sizes, the pressure drop was found to decrease by several times. It was expected that the straight through pores would have superior performance as compared to the fibrous and networked membranes. Several explanations for its unexpected performance are given here. First, since the laser ablation process is a thermal process, it is expected (and can be verified with microscopy) that the surface roughness on the inside of the hole is greater than the surface roughness of either the woven or the fibrous membranes. This observation might provide additional insight as to why the fibrous membranes perform better than the networked membranes. At small pore sizes, the pressure drop effects of surface roughness are magnified if the flow is turbulent. A second explanation comes from the observation that some variation in pore size might exist across the membrane. While the initial results of pore size across the membrane are encouraging, it is impossible to check all 22,500 pores on the membrane. Prior tests have shown that if the membrane is not within its required flatness, the out-of-focus can cause large variations in pore size including elimination of the pores altogether. Additional methods are being investigated to minimize workpiece flatness prior to laser processing.

Micromolded Approach – Silicon wafer substrates were chosen to spin coat SU8. A photomask of hole arrays consisting of 5-micron diameter holes on 100-micron spacing was used to expose the resist to create a SU-8 mold (Figure 3c shows a 45 degree view of the posts). PDMS is then spincoated into the SU8 micromold (see Figure 3d) and then the PDMS membrane is released.

Several membranes were fabricated with aspect ratios as high as 3:1. However, no flow was reported in any of the membranes as the minimization of energy in the membranes with 5 micron holes (in nitrogen and air) caused the holes to collapse. In the future, stiffer PDMS formulations will be considered to avoid the sealing of the pores to themselves.

CONCLUSIONS

Based on test results to date, we have found that, in general, woven pore membranes have much higher mass transfer rates than all other membranes. We have classified commercial membranes into three key classes: woven, fibrous and networked. We have developed an initial normalization procedure for comparing the results of various tests. Also, we have found that the laser micromachining technique improves the mass transfer rate in general but that the mass transfer properties are much less than those found for woven membranes. Conventional PDMS technology was not found to support membranes with such high aspect ratio. Future work could involve the formulation of membranes with stiffer PDMS properties.



a) b) c) d)

Figure 3. a) Front of pore array with 100 μm spacing and average pore size of 16.5 ± 0.5; b) Back of pore array with 100 μm spacing and average pore size of 5.3 ± 0.8; c) Micrograph of 5μm diameter posts with a height of 65μm (1:13 aspect ratio) on a silicon wafer; and d) PDMS spincoated onto SU8 micromold with a height of approximately 35 μm.

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