DEVELOPMENT OF INORGANIC MEMBRANES FOR HYDROGEN SEPARATION

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ABSTRACT

The purpose of this work is to improve the method of fabricating tubular metal supported microporous inorganic membranes. Earlier work focused on the original development of inorganic membranes for the purification of hydrogen. These membranes are now being scaled up for demonstration in a coal gasification plant for the separation of hydrogen from coal-derived synthesis gas for a project funded by the Office of Fossil Energy's Gasification and Coal Fuels programs [1]. This project is part of FutureGen, an initiative to build the world's first integrated sequestration and hydrogen production research power plant. Although previous work in the Advanced Research Materials Program project led to development of a tubular metal supported microporous membrane which was approved by the Department of Energy for testing, the membranes generally have lower than desired selectivities for hydrogen over other gases common in synthesis gas including carbon dioxide. The work on this project over three years will lead to general improvements in fabrication techniques that will result in membranes having higher separation factors and higher fluxes. Scanning electron microscopy and profilometry data will be presented to show qualitatively and quantitatively the surface roughness of the support tubes. We will discuss how the roughness affects membrane quality and methods to improve the quality of the support tube surface.

INTRODUCTION

The purpose of this work is to improve the method of fabricating tubular metal supported microporous inorganic membranes. Earlier work focused on the original development of these membranes which are now being scaled up for demonstration in a coal gasification plant for the separation of hydrogen from coal-derived synthesis gas for a project funded by the Office of Fossil Energy's Gasification and Coal Fuels programs. Although previous work lead to development of a tubular metal supported microporous membrane based on ORNL technology which was approved by the Department of Energy for testing, the membranes generally have lower than desired selectivities for hydrogen over other gases including carbon dioxide. The work on this project over three years will lead to general improvements in fabrication techniques that will lead to membranes having higher separation factors and higher fluxes.

EXPERIMENTAL

Previous work has shown that high selectivities for helium or hydrogen over carbon dioxide can be achieved and that the permeance of helium and hydrogen increases with increasing temperature. At 250°C, the ideal separation factor for a ceramic supported membrane was 48.3. As a result of the lower temperature required for the separation of hydrogen in the Integrated Gasification Combined Cycle (IGCC) concept plant, a switch was made to metallic supports. Metallic supports are more robust when compared to ceramic supports and can be sealed into membrane modules more easily by welding or brazing. A transmission micrograph of a stainless steel support membrane is shown in Figure 1. The dark area is the stainless steel type 316L support tube which has a thickness of approximately 500 µm and a pore-size of approximately 5 µm. The layer directly on top of the support tube is an intermediate layer (gray in color) having a pore-size of 7 nm with an average thickness of 2-3 µm. The top separative layer (white) is approximately 0.5 µm thick and has a pore-size less than 1 nm. These membranes made using metallic supports have had somewhat lower selectivities and data has also shown that membranes produced using supports made from water atomized metal powers had lower selectivities than membranes produced using supports made from gas atomized powder. It is believed that these lower selectivities are due to imperfections in the support tube that result in pin-holes or over-sized pores in the subsequently applied membrane layers. Scanning electron micrographs (SEM), at a 60° to the surface, of supports made from water atomized stainless steel powder and gas atomized stainless steel powder are shown in Figures 2 and 3. Figure 2 shows the roughness of the surface from the irregularly shaped particles made by water atomization while Figure 3 shows a smoother surface from the spherical particles made by gas atomization. While Figure 3 shows a smoother surface, there are still some surface irregularities due to the larger particles protruding from the surface. Since the intermediate layer is only approximately 2-3 micrometers thick, the intermediate layer would have a difficult time smoothing out the surface of a support tube made from water atomized powder. This layer is now the support structure for the very thin nanoporous separative layer. Without a smooth intermediate layer, it would be difficult to fabricate membranes having no leaks in the separative layer. Therefore, much of our effort to date has been quantifying the smoothness of the support surface as a function of tube forming properties and correlating these properties to the performance data of completed membranes.

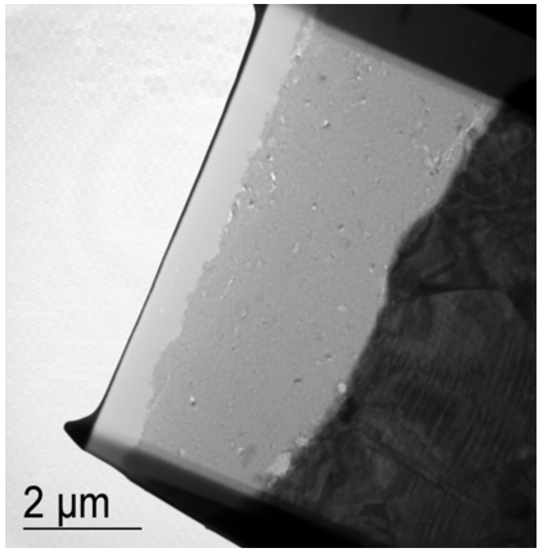

Figure 2 Transmission micrograph showing the support tube (dark), intermediate aluminum oxide layer (gray), nanoporous separative layer (almost white), and sputtered metal layer added to aid in sectioning.

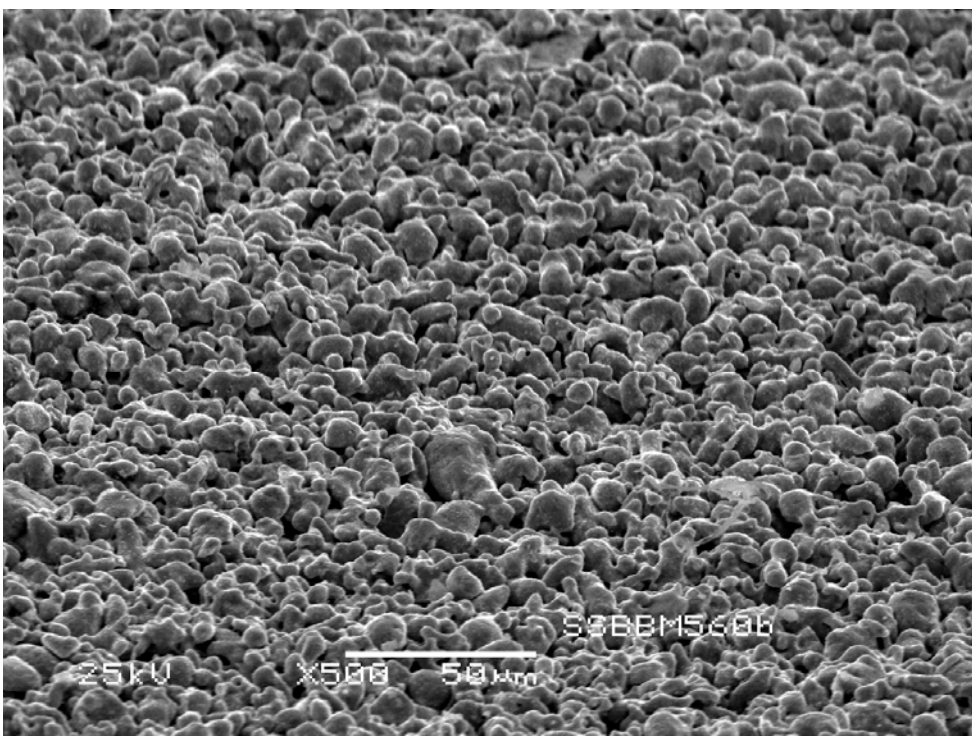

Figure 1 SEM of inside surface of support tube made from water atomized powder taken at 60°.

Profilometry of the surface of the support tubes has been initiated using a software product called MeX from Alicona Imaging. This software works with SEM images taken at various tilt angles to evaluate the roughness of the surface along an axis. This analysis is being used to correlate measured surface roughness with membrane properties and powder properties used to make the supports. Figure 4 shows how the software can use colors to illustrate the height of particles and the depths of the valleys. While the image of the support made from water-atomized powder contains bright pinks and purples (indicating particles protruding high above the surface and orange/yellow areas, (indicating deep valleys), the image of the support made from gas-atomized powder contains mostly light blues and greens indicating a more uniform surface. Figures 5 and 6 show an analysis along an arbitrary line drawn across the samples. Although placement of the line is very subjective, this analysis shows that the peak-to-valley distances are greater in the supports made from water-atomized powder.

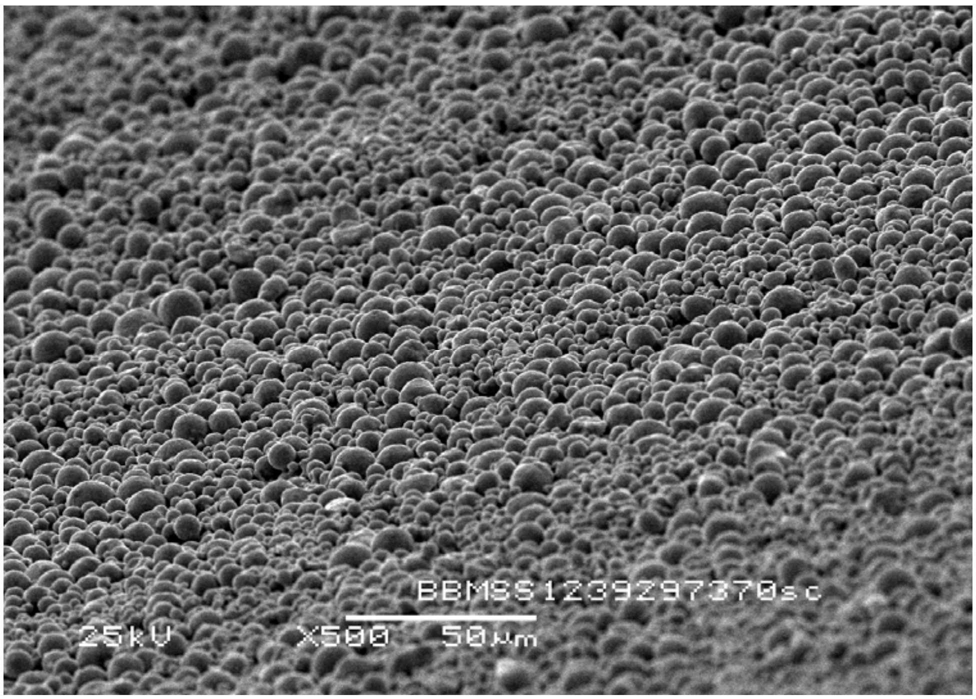

Figure 3 SEM of inside surface of support tube made from gas atomized powder taken at 60°.

Performance
Membranes fabricated using supports made from gas atomized powder were tested at the National Energy Technology Laboratory (NETL) in Pittsburgh, PA as part of a project to scale up ORNL's hydrogen separation membranes. The selectivities for hydrogen over carbon dioxide were usually found to be less than 5 at temperatures below 200°C but increased to as high as 48 when the temperature was increased to 300-450°C. Results for one of the membranes are shown in Figure 7. The large increase in selectivity is mostly due to a large increase in the permeance of hydrogen as the temperature is increased.

FUTURE WORK

Samples of gas atomized powder in varying particle size have been procured. Also, a sample of a gas atomized stainless steel powder having a narrower particle size distribution than our earlier as-received powders has been procured. This powder is essentially the same as the powder used to fabricate the tubes shown in Figure 3 with the largest particles removed leaving particles mostly less than 10 micrometers in diameter. When these tubes are formed, we will evaluate the supports for surface roughness, apply membrane layers and measure for the quality of membrane layer, mainly leak rate.

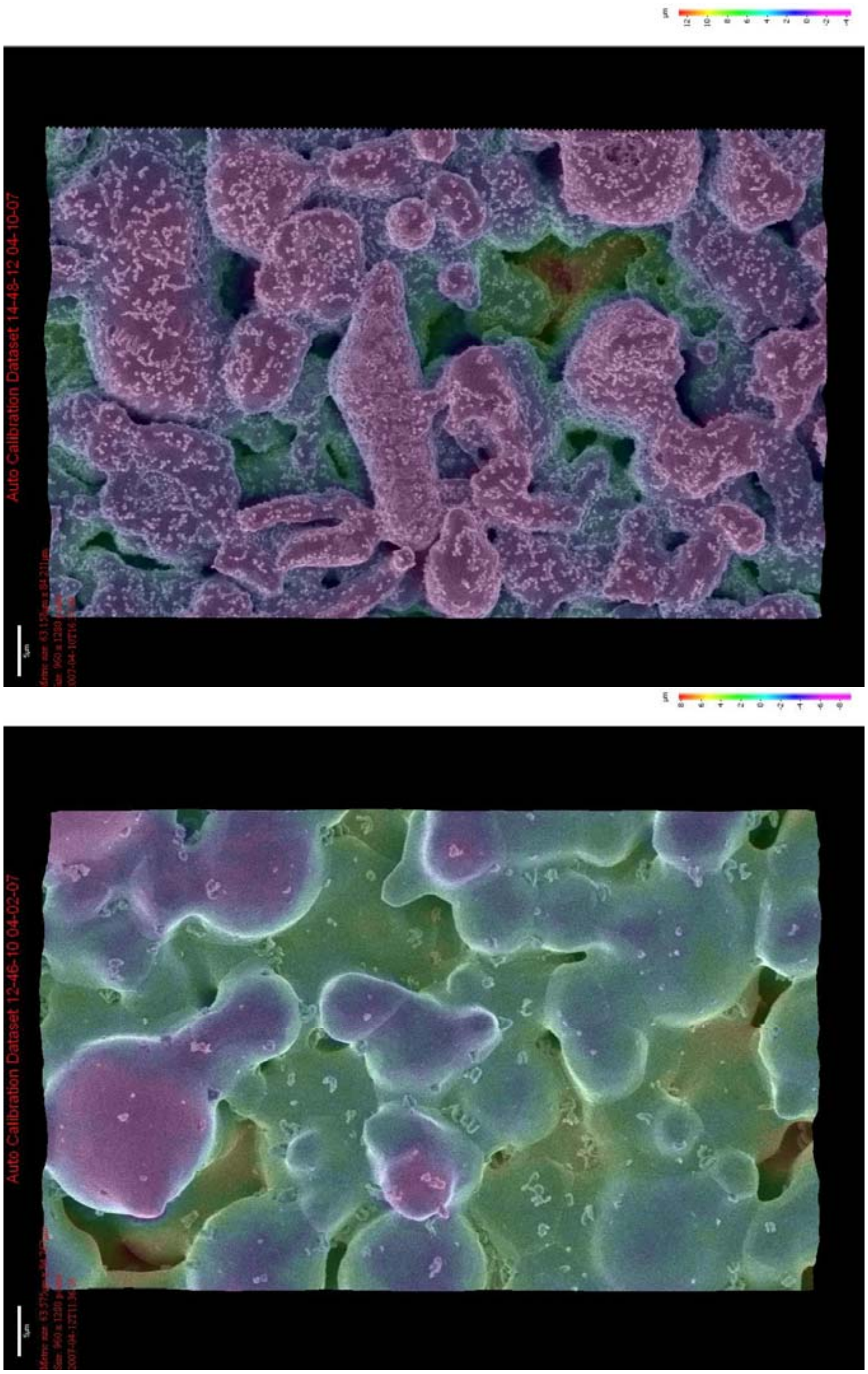

Figure 4. Colors help identify peaks and valleys of support. Contrast in colors for support made from water atomized powder (upper) shows larger peak-to-valley distances than support made from gas-atomized powder (lower).

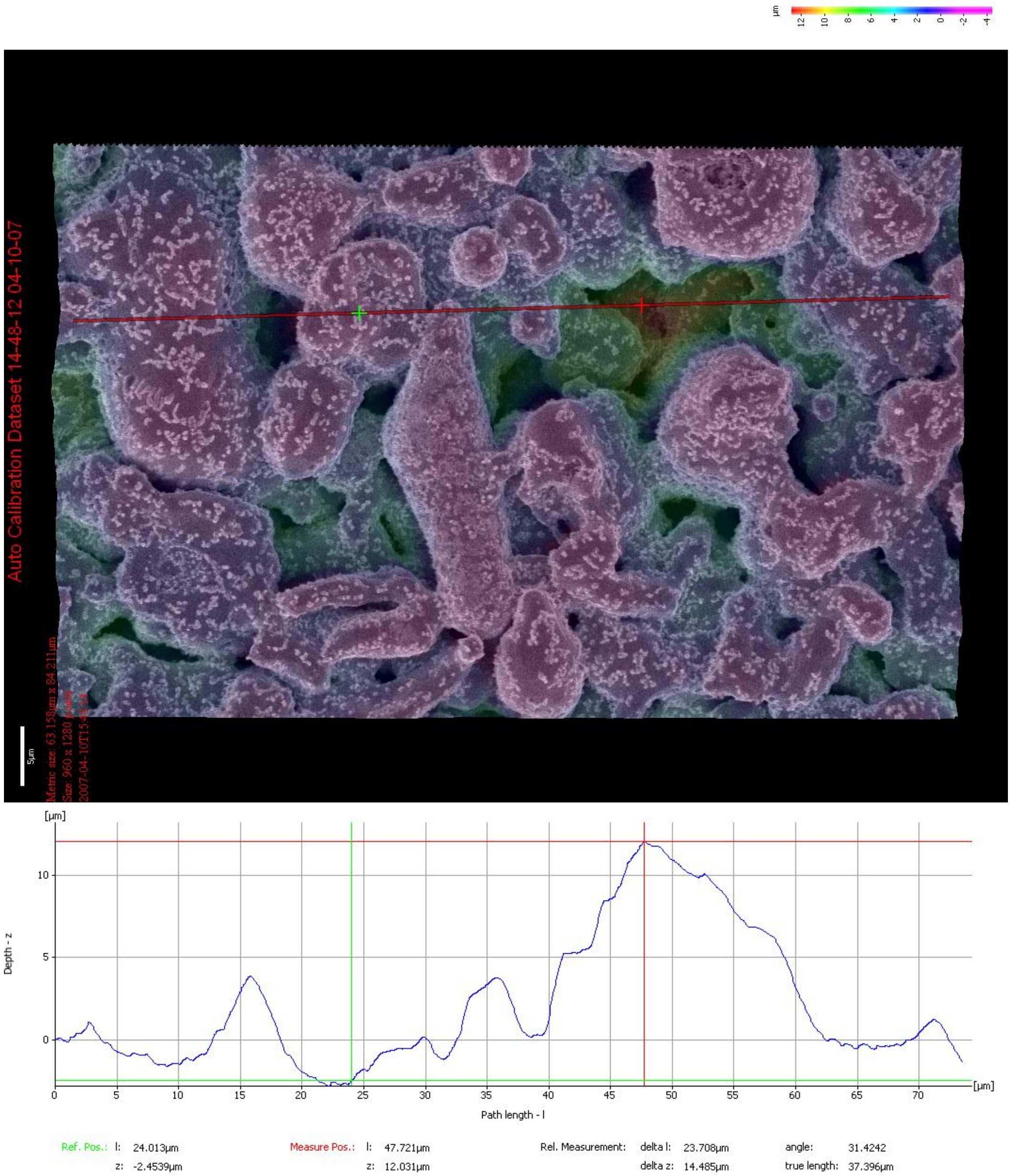

Figure 5 Linear analysis of surface made from water-atomized powder shows large peak-to-valley transitions.

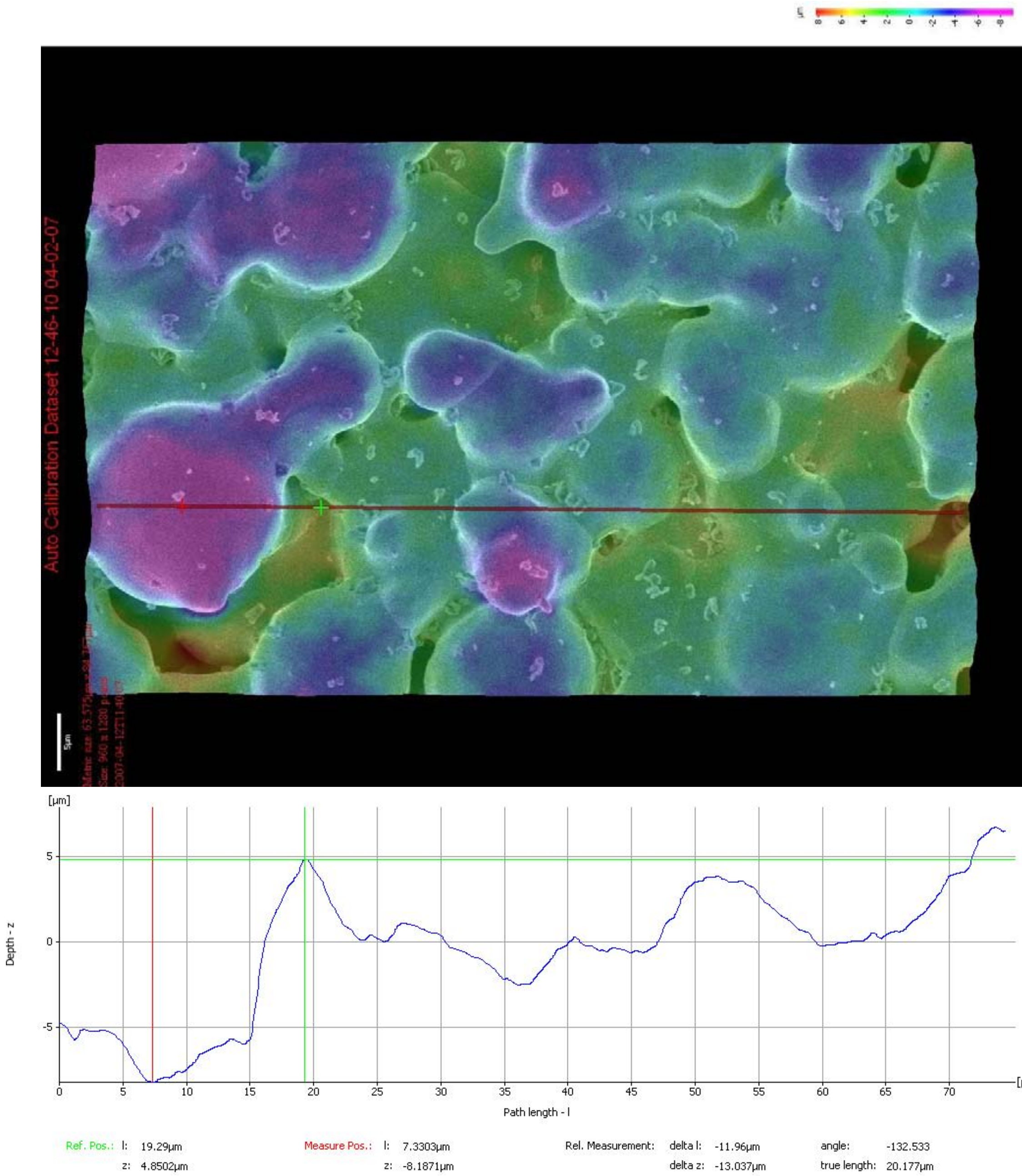

Figure 6 Linear analysis shows smaller peak-to-valley transitions in supports made from gas-atomized powder.

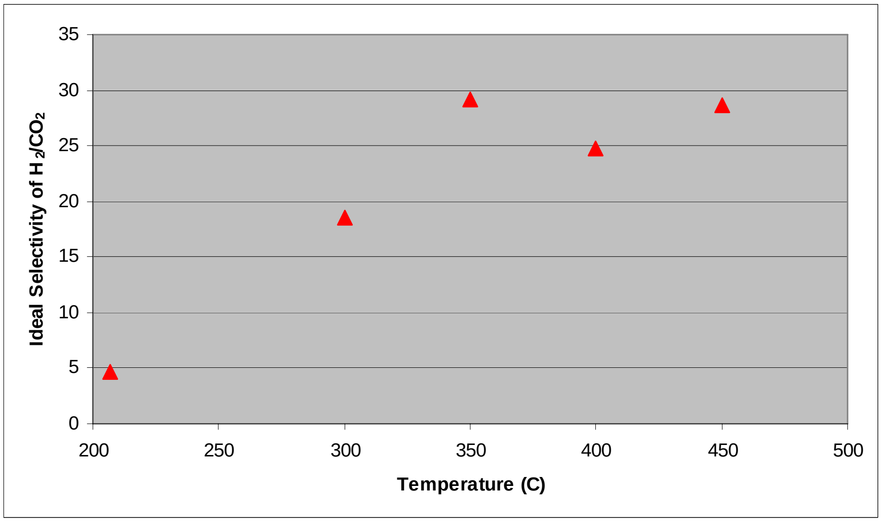

Figure 7 Pure gas selectivity (ratio of pure gas permeances) of hydrogen over carbon dioxide measured at NETL as part of Scale-up Project

REFERENCES

1. Judkins, R.R.; Bischoff, B.L., "Scale-Up of Microporous Inorganic Hydrogen-Separation Membranes," *Proceedings 22nd Annual International Pittsburgh Coal Conference, Sept. 12-15, 2005*.