Title: HIGH TEMPERATURE EFFORTS AT LOS ALAMOS NATIONAL LABORATORY

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With the potential for significant payoffs in chemical processing, separation science, and "green technology", inorganic membranes merit the increased attention they are currently receiving. Application of thin film deposition and characterization expertise at Los Alamos National Laboratory (LANL) to the fabrication of membranes has led to the development of two new membranes. The first is a zeolitic film formed by pulsed laser deposition (PLD). The material deposited is largely amorphous but yields an interesting microporous structure. The pores, roughly 10 to 15 Å in diameter, run perpendicular to the substrate and, since the film is typically only a half micron thick, provide excellent flow rates. The PLD material has been deposited on quartz crystal microbalances (QCMs) to investigate its potential as a sensor. As such, it has shown discrimination of simple alcohol isomers. The second membrane, consisting of a composite metal structure, passes hydrogen exclusively. Currently, we are studying the possibility of incorporating the membrane in a hydrogen fuel cell using a methanol reformer.

I. Pulsed Laser Deposition of Zeolitic Materials

The predictable microporosity combined with the well-defined shape of the zeolite cage have made this material one of the most widely used catalysts in the chemical processing industry. Consequently, the incentive for constructing a zeolite membrane for use in separation and catalytic processes is quite high. For such a membrane to be useful, it must be pinhole-free, thin enough to provide high flow rates, and economical to produce. Various attempts to achieve these goals include attaching zeolite crystals to gold surfaces using thio-organo-silane coupling layers, embedding zeolites in a metal foil, or incorporating them in an epoxy or silica matrix. Zeolites have also been constructed on various supports or as free-standing films. Unfortunately, most of the films developed to date do not meet all of the above-mentioned requirements. In the ongoing...
search for such a membrane, we have investigated pulsed laser deposition (PLD)\(^9\) of zeolites. Using this technique, a pulsed laser beam is focused on a target, vaporizing the material which subsequently is deposited onto a substrate. The mechanism can be explained by reactive particle transfer. The impinging laser creates a plume of particles at the target that consists of monatomic and diatomic neutrals as well as reactive clusters.\(^{10}\) When the target is crystalline, the clusters may be composed of several unit cells having reactive edges or dangling bonds. Using the zeolite as a target, the deposited films consist of porous zeolite material connected by amorphous, microporous material.

The experimental apparatus for the PLD of the zeolitic material is shown in Figure 1. A pulsed Nd:Yag laser (XL-81 Continuum, \(\lambda = 532\) nm) emitting 6 nsec pulses was used as the ablating laser. The pulse frequency was 5 Hz while the focused beam yielded a laser fluence of 0.9 J/cm\(^2\). Both the target and substrate were rotated continuously during the deposition to improve uniformity of the films. An oxygen pressure of about 140 millitorr of oxygen was maintained in the chamber. Films were deposited on silicon substrates for evaluation by electron microscopy and on QCMs for evaluation of molecular selectivity in sensing devices. The faujasite targets used in the depositions were provided by Dow Chemical. Deposition times of 30 minutes typically produced films that were 0.4 to 0.5 \(\mu\)m thick.

![Figure 1](image)

**Figure 1** The PLD experimental setup.

Investigation by transmission electron microscopy (TEM) revealed that, although some crystalline material existed in the films, they were largely amorphous. The diffraction pattern of the crystallites was compared with that of the target material and they appear to be consistent with one another. Apparently, zeolite crystallites are transported from the target to the growing film in the ablated plume. Nevertheless, the more interesting aspect of the film is the porous structure of the amorphous material. A cross-section view of the film deposited on silicon is shown in Figure 2. Estimating the pore sizes from the TEM photo show that they appear to be about 10 to 15 \(\AA\) in diameter. This is considered to be in the microporous regime where molecular sieving can begin to occur. Furthermore, the pores are largely oriented perpendicular to the substrate. This allows high flow rates through the films when deposited on porous substrates. Presumably, the microporous material results from the buildup of clusters of partial zeolite cages. It is noteworthy that the observed pore diameters in the amorphous material are similar to that of the parent zeolite.
Figure 2  Cross-section view of the PLD zeolitic thin film material deposited on silicon.

One of the first applications for which the zeolitic thin film were tested was that of sensors. This was done by depositing material on QCMs and then introducing various small chain alcohols and measuring the frequency response. The measured change in frequency can be related to the mass of the substance adsorbed to the surface. These measurements are described in greater detail elsewhere\textsuperscript{13}. As shown in Figure 3, the films were able to discriminate between isomers of propanol. Similar results were obtained for butanol isomers.

The application of the PLD zeolitic thin films to sensor technology has provided encouraging results. Distinguishing between the subtle structural differences of short chain alcohols suggests that these materials may indeed be useful as sensing devices. The chemical composition and structure of this material will allow implementation of sensors at elevated temperatures or in chemically harsh environments.

The evaluation of these films as membranes is the focus of current research. Although the majority of the deposited material is amorphous, it yields a microporous structure having not only high porosity but pores oriented perpendicular to the substrate. This results in remarkable gas fluxes through the material. Due to the high gas flow rates, the testing system is requiring modifications to accommodate the necessary measurements.
11. Composite Metal Membrane

While the PLD zeolitic films are porous structures, capable of separation of molecules based on size, the metal membranes are dense structures, allowing only hydrogen to pass through its lattice. The most popular metal currently used for pure hydrogen separation has been palladium or one of its alloys. Several problems have limited its more widespread use. First, palladium or palladium/silver alloys are expensive. The cost issue alone has greatly limited its usefulness for many large scale processes. Even for applications where the materials investment can be justified, the embrittlement problems associated with extended use have further restricted its use. Finally, a membrane structure consisting only of palladium or palladium/silver does not pass hydrogen very rapidly. A membrane that is thick enough to provide the necessary mechanical stability will inherently have low permeation rates. The composite metal membrane is an attempt to effectively address all three major issues restricting use of palladium based membranes.

Palladium is not unique in allowing atomic hydrogen to pass through its lattice. Indeed, other metals such as the group 5 materials can provide substantially higher fluxes of hydrogen\textsuperscript{14}. They, however, suffer from other hindrances. Not only do these metals not catalyze the dissociation of molecular hydrogen at their surfaces, they also form oxide layers, impeding the flow of hydrogen. The composite structure mates the surface catalysis of palladium with the structural integrity and improved flow rates of a group 5 refractory metal to form a hybrid membrane that resists embrittlement, has high gas fluxes, and is relatively inexpensive. While this concept is certainly not unique\textsuperscript{15,16}, the application of vacuum thin film technology in the fabrication of the structure has resulted in improved membrane performance.

Fabrication of the membrane began by mounting a refractory metal such as tantalum, niobium, or vanadium in a vacuum chamber. The metal surface was cleaned by ion beam sputtering. This removed any surface impurities along with the ever-present metal oxide layer. Following the sputter cleaning, the metal foil was immediately coated on both sides with palladium.

Figure 3  The relative amounts of gaseous components adsorbing onto the PLD coated QCMs as a function of partial pressure.
in the same chamber. Since the vacuum was not broken between the sputtering and coating processes, the palladium was deposited on a clean surface, providing an interface across which the hydrogen atoms could readily move. The palladium was deposited using either electron beam evaporation or ion beam sputtering of a palladium target. The central metal foils used in the construction of the membranes were typically from 10 to 100 μm thick while the palladium layer was 1 μm or less. Coated foils were studied using x-ray diffraction (XRD) prior to and following hydrogen permeation tests. The palladium layer was found to be predominantly oriented with its (111) crystallographic axis normal to the plane of the foil surface. It was also observed that usage of the membrane improved the crystallinity of the palladium layer.

To test the membranes, the foils were pressed between two copper Conflat® flange gaskets, one of which was fitted with a porous brass support to keep the foils from breaking upon the application of gas pressure. The area of the membrane exposed to the gases was 2 cm². The vacuum flanges were mounted on a stainless steel tube as shown in Figure 4. The gases that were used for the test mixture were 50:50 argon-hydrogen and a simulated methanol reformed gas (74% hydrogen, 25% carbon dioxide, 1% carbon monoxide). Most of the testing was done using the argon-hydrogen mixture and the residual gas analyzer (RGA) used to monitor the permeate stream. Detection of significant levels of argon in the permeate stream indicated a ruptured or improperly sealed membrane.

![Figure 4](image)

**Figure 4**  The permeation apparatus. Temperature of the membrane was controlled by a heater controller. The permeate flow rate was measured with a mass flow meter.

The results of the hydrogen permeation measurements are displayed in Figure 5. In the experiments summarized in Figure 5, the upstream gas was an argon/hydrogen mixture (50:50). The measurements taken with the foil having 1 μm palladium deposited on each side were obtained using 790±2 torr upstream pressure. The resulting downstream pressure varied from 33 torr for the lowest temperature measurement to 43 torr for that at the highest temperature. The data
designated by the filled squares in Figure 5 was obtained using a feed pressure of 710±2 torr while the downstream pressure was maintained at 30±2 torr. The experimental conditions under which the other data points were obtained were similar to those listed above. The observation that the flow rates for the membranes coated with 0.5 μm of palladium on each side is approximately double that of the 1.0 μm palladium coated foils suggests that the central tantalum layer is not significantly impeding the flow. This is further supported by the flows through the membrane having a 100 μm tantalum layer. The scatter in the various membranes coated with 0.5 μm of palladium is largely due to differences in the surface texture of the tantalum foil. We have observed that a slightly rougher foil surface will yield overall flow rates that are somewhat higher than those resulting from a foil having a smooth surface. This is due to the increased surface area on the rougher textured foils. The effect of various surface treatments is the focus of ongoing investigations. Indeed, manipulation of surface effects may allow the fabrication of membranes with even better hydrogen fluxes.

The minimum thickness of palladium on the refractory metal necessary to provide improved hydrogen fluxes has not yet been experimentally determined. Nor has the maximum thickness of the refractory metal been established. Nevertheless, Steward's data\textsuperscript{14} suggest that at 300°C, the refractory metals provide approximately two orders of magnitude higher hydrogen fluxes than does bulk palladium.

![Graph](image)

**Figure 5** Results of the hydrogen permeation measurements for several membranes of varying Ta and Pd thicknesses. Hydrogen flux is measured in standard cubic centimeters per minute (sccm).

To study the effects of prolonged usage of the composite membrane, a 25 μm thick foil coated with 1 μm of palladium on one side and 0.5 μm on the other was mounted in the testing apparatus. An argon/hydrogen gas pressure of 772 torr was applied to the upstream side of the membrane while the downstream hydrogen pressure was maintained at 23 torr. This membrane was run continuously for 100 hours at a temperature of 287°C yielding the results displayed in Figure 6. In the latter stages of the experiment, the flows stabilized at 31 sccm. The initial decrease in hydrogen flux is consistent with what has been observed for previously reported composite membranes\textsuperscript{16}. This may result from the improvement in crystallinity with membrane usage that was observed in the XRD results. Previous studies of thin films of palladium deposited
on tantalum surfaces suggest that surface defects are important in the absorption process\textsuperscript{17}. Movement or elimination of such surface defects may actually slow hydrogen permeation.

![Graph](image)

**Figure 6** Flow results from a membrane run continuously for 100 hours.

With the interest in alternate energy sources, fuel cells have seen renewed interest in recent years. The carbon monoxide fouling problems observed in the hydrogen fuel cell have been problematic for the use of reformed fuels in these devices. It is thus fitting that one of the first applications being seriously considered for the composite metal membrane is the exclusion of all products coming from the fuel reformer into the fuel cell save hydrogen. To test the membrane with a simulated methanol reformed fuel mixture, a mixture of H\textsubscript{2}/CO\textsubscript{2}/CO (74:25:1) was introduced to the membrane at 287°C. The hydrogen fluxes were monitored for almost 30 hours and the fluctuations in flow rates were similar to those observed for the membrane operating in the H\textsubscript{2}/Ar gas mixture (Figure 5).
REFERENCES
