ISSUES AFFECTING THE RELIABILITY OF PALLADIUM MEMBRANE HYDROGEN PURIFIERS

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I. INTRODUCTION

The production of reliable streams of ultra-pure hydrogen (UHP) is an essential enabling technology of the compound semiconductor industry. The term *ultra-pure* is understood here to refer to hydrogen gas in which total impurity concentration is below the parts per million (ppm) level. To achieve this level of purity, it is necessary to make use of a purification system, which can accept industrial grade hydrogen as a feedstock to produce UHP at its point-of–use. The principal method of UHP production adopted by the compound semiconductor industry is based upon the diffusion of gaseous hydrogen through tubular membranes composed of a 23-atom % silver- palladium alloy, which allow for both high fluxes and high permeation selectivity. The key to accounting for both of these characteristics is the catalytic splitting of molecular hydrogen [(1)]. The resulting hydrogen atoms are adsorbed on the membrane surface, rapidly absorbed into the metallic lattice and diffused to the opposite surface where they recombine to form molecular hydrogen which is released to the permeate stream. The fundamental chemistry and physics of the foregoing process has been studied for well over 100 years and continues to be of interest currently [(2,3,4)] and the first commercial version of a hydrogen purifier operating in this manner was developed by the Johnson Matthey (JM) in the 1960's. In 1995 Power and Energy (P&E) introduced a commercial palladium-based hydrogen purifier, which retained some of the basic features of the JM system but drastically modified its engineering design. The performance and characteristics of the P&E Hydrogen Purifier is the central concern of this paper.

II. QUALITY CONTROL: AVOIDANCE OF LEAKS

By far, the most important issue involved in the design of any palladium hydrogen purifier is elimination of latent leakage and subsequent loss of purity in the permeate stream. Quality control of *all* components is important, but avoidance of pinholes in the tubular membranes and leaks through brazed joints connecting the membranes to stainless steel tubing is especially a matter of concern. The latter is commonly encountered in hand brazing or when multiple membranes are inductively brazed at the same time. It is, however, solved by using a patented technique involving symmetrical brazing, high-vacuum, high-melting brazing material and computer-control.

The problem of pinhole avoidance and detection results mainly from the inadequate quality control exercised in fabrication of the tubular membranes in which inclusions of extraneous materials are often encountered. These inclusions result in defects leading to pinholes. Since the probability of encountering a pinhole is directly proportional to the concentration of inclusions and inversely proportional to membrane thickness, metallurgical quality ultimately places a practical lower limit (typically 0.01-0.05 mm) on membrane thickness. Rejection rates as high as 50% have been encountered and are known to vary widely from one supplier to another. The problems stemming from inclusions are further compounded as a result of the coiling of tubular membranes into space-saving helical configurations. In the case of the P&E membrane system, straight tubular membranes are subjected to carefully fabrication process. This patented process is designed to insure uniformity of both wall thickness and tension on the helix. A benefit of this technique is a significant increase in the probability of detecting pinhole formation over and above that of straight tubular membranes. This ability results in significantly greater reliability per membrane and therefore the diffusion cell.

III. INSIDE-OUT VS OUTSIDE-IN

A unique design feature of the P&E Hydrogen Purifier is its "inside feed" design,(5) which calls for the admission of high pressure feed hydrogen to the *inside* of a tubular membrane. The flow is thus to the outside of the membrane where the diffused H atoms recombine to form UPH which then flows to the point of use while the impurities in the feed remain behind and are then vented thru a bleed to the atmosphere. Virtually all of the hydrogen in the feed gas diffuses through the membrane; only 1 or 2% of it flows out of the bleed along with the flushed impurities. This self-cleaning feature of the P&E membrane minimizes accumulation of impurities that could possibly interfere with the catalytic action on the inside membrane surface. There are several significant advantages of the inside-out design when employed in conjunction with coiled tubular membranes. As a result of the combined stretching and coiling process, the convex surface of the tubular membrane is in tension whereas its concave surface is in compression. The resulting tendency of the tube to collapse is, however, offset by the positive pressure differential between its inside and outside walls. The conventional design (outside–in) requires use of an interior stainless steel supporting spring which may act as a source of impurities. This spring may also reduce the UPH output over time as a result of the crimping of the membrane against the spring, thereby effectively reducing its inner surface area.

The enhancement of tubular rigidity conferred by the inside-out design has the added advantage of allowing for larger inside diameters for a given wall thickness and the ability to have a self-supporting membrane. As noted previously, leak avoidance is a very high priority in the design of a hydrogen purifier. With proper quality control we can assume that a freshly minted membrane is leak-free. However, to ensure long-term reliability of the fully assembled purifier, a detailed analysis is required to determine the robustness of the purifier in the face of challenges such as thermal shocks, mechanical stresses, vibration, large flow swings and pressure surges, all of which are encountered in the course of thousands of temperature and pressure cycles over periods ranging from months to years.

The crucial design feature related to the foregoing problems results from the necessity to totally avoid contact between a hot membrane surface and another body. Similarly, maintenance of helical rigidity is required to avoid self-collision. These requirements impose severe constraints on parameters such as helical pitch, radius of curvature and the ratio of helical to tubular diameter. The nesting of multiple tubular membranes in the cylindrical space surrounding the membranes further exacerbates the problem of meeting these requirements.

IV. PRESSURE FLUCTUATIONS

An important challenge to long-term purifier operation results from pressure surges generated inside the diffusion cell by cyclical opening and closing of valves admitting

UPH to the point of use. Figure 1 depicts the pressure variations on the UPH side (the outside) of the membrane, the assumption being that the feed pressure inside the membrane is externally regulated (typically at 20 Mpa) and therefore constant throughout the cycle.

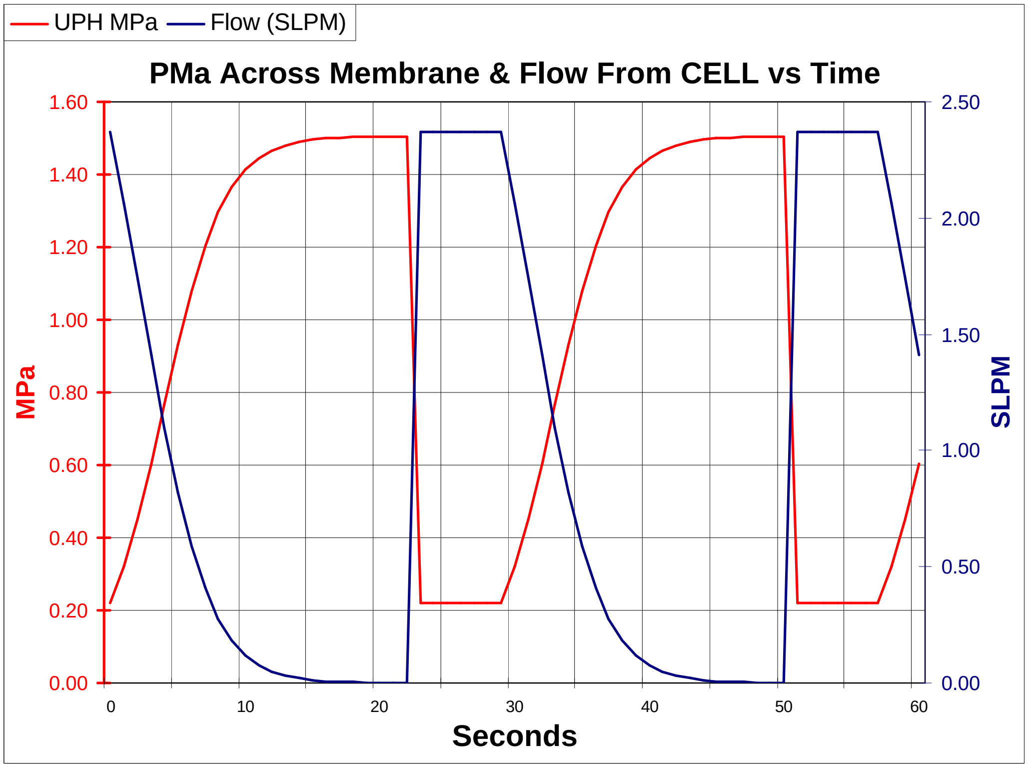

FIGURE 1

When the purifier is delivering UPH to the point of use, the pressure on the UPH side is typically about a 0.2Mpa. When the UPH outlet valve is shut, the pressure on the UPH side rises steadily at a rate governed by the diffusion rate through the membrane, which is proportional to the difference between the square roots of the fixed inside pressure [2] and the increasing outside pressure. This process continues until the inside and outside pressures equalize.

Now consider the effect of re-opening the UPH outlet valve, thereby creating an instantaneous pressure gradient, of approximately 1.2Mpa between the space surrounding the UPH side of the membrane and the point of use. The repeated dissipation of pressure impulses caused by an asymmetrical exit orifice on the diffusion cell will degrade the palladium membranes. This problem of an asymmetrical exit orifice is obviated by the inclusion in the cell of a perforated central collection tube. This feature distributes the forces created by an exit pulse over the length of the diffusion cell, reducing its effect on any membrane by more than two orders of magnitude and creating a uniform low-stress environment in all dynamic flow conditions.

V. POWER FAILURE

It is well known that conventional palladium-based hydrogen purifiers are prone to high rates of irreversible membrane damage as a consequence of unexpected interruptions of power. Because both the feed hydrogen inlet valve and the UPH outlet valve of the purifier require power in order to remain in the open position, the effect of an abrupt loss of power is that both close. Cooling then ensues while the palladium alloy is saturated with absorbed atomic hydrogen. The volume increase accompanying absorption of hydrogen in the palladium crystal matrix leads to accumulation of strain energy in the lattice(2). In these circumstances lattice contraction may be too rapid to allow for adequate stress relaxation, the possible result being hydrogen embrittlement and membrane fracture.

The point to be made here is that the problem of power failure in palladium membrane purifiers is readily solved by incorporating certain features routinely found in P&E hydrogen purifiers. In fact no P&E purifier has ever failed as a result of power failure. The key to the solution of this problem is to drain the membrane of most of its hydrogen as soon as possible but in a controlled manner. As hydrogen ceases to flow into the feed side of the membrane, the bleed comes into play as it vents the hydrogen from the feed side into the atmosphere. In the worse case, power fails when UPH side is at maximum pressure, i.e. equal to the feed pressure. The amount of hydrogen in the diffusion cell is now at a maximum and the thermal energy in the heater is at a minimum. As flow through the bleed ensues, the hydrogen on the UPH side will back-diffuse at a rate governed by both the diffusion rate of the membrane and the flow rate through the bleed. If at the moment of power failure, the UPH is in its low-pressure phase, the hydrogen on the feed side will continue to flow in its normal direction until the flow to the UPH side is exactly balanced by the flow out of the bleed. Then the flow will reverse until most of the hydrogen in the system has drained thru the bleed. Concurrent with either of these situations, a nitrogen valve, which is normally shut, will open by default and flush the feed of the membrane.

VI. CONCLUSION

Issues governing the performance and reliability of the palladium purifier have been discussed in moderate detail. These fall into two related but distinct categories, namely (1) properties and performance of materials and (2) engineering design. The most pressing materials issue is the detection and elimination of defects in the membrane. Attention to this issue is essential. However, the overall performance of an operational purifier depends equally on the details of the engineering design, which insure that the components are completely compatible. Avoidance both of potentially damaging contacts between stainless steel and the membranes and of collision within the diffusion between membranes, together with the need to conserve space, imposes severe engineering design constraints. The seriousness with which these details are addressed determines the reliability and life expectancy of palladium based hydrogen purifiers.

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