Hydrogen Diffusion Technology

COMMERCIAL APPLICATIONS OF PALLADIUM MEMBRANES

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The technology for extracting pure hydrogen from hydrogen-rich gas mixtures by diffusion is now well established. The success of the process and the demand for the product has led to the formation of Johnson Matthey Equipment, a company devoted to the supply of equipment based upon the properties of the platinum group metals, principally hydrogen purification and generation equipment.

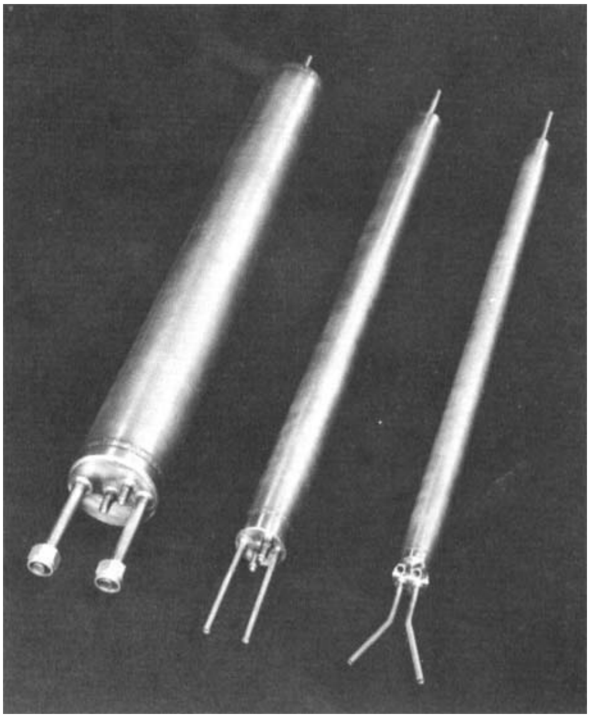
The original work on the diffusion of hydrogen through palladium was carried out by Thomas Graham in 1866, when he was Master of the Royal Mint, in London (1). However, for many years the commercial use of palladium as a hydrogen diffusion membrane was seriously inhibited by the fact that at relatively low temperatures the adsorption of hydrogen into palladium induces an $\alpha \rightarrow \beta$ phase transformation, which consequently changes the atom spacing in the metal lattice. This dimensional change is large enough to distort the palladium membrane to such an extent that after only 30 hydrogenation-dehydrogenation cycles very little of the original structure remains. As a consequence of this, purification of hydrogen using a palladium membrane was only possible if the membrane was kept above a critical temperature of about 300°C throughout its working life, a requirement that did not favour its commercial use.

It was nearly a century after Graham's discovery that Dr. J. B. Hunter, while working on the diffusion of hydrogen through palladium alloys, found that the maximum rate of hydrogen diffusion through silver-palladium alloys occurred at a composition close to the maximum solubility of silver in palladium (2). Unexpectedly the alloy was found to be stable when thermally cycled through the $\alpha - \beta$ phase transition temperature in the presence of hydrogen. Furthermore the addition of silver made metal fabrication easier as well as reducing the intrinsic value of the alloy. This was a major step forward and led to the development of a range of commercial diffusion cells.

Early hydrogen diffusion equipment was of a simple design. Fabricators of the platinum group metals rarely make a complete product. Generally they are involved in supplying components which are often intricate and complex in design, but which comprise only a part of the complete product. Thus when fabrication of hydrogen diffusion equipment commenced only the diffusion cells were made; market indications suggesting that potential purchasers would want to construct diffusion plants to their own design, or to incorporate diffusion cells into existing plant. The diffusion cells were of robust construction and had an output of 1 to 500 standard cubic feet per hour (approx. 0.03 m^3/h to $14 m^3/h$). They were designed to operate at temperatures of 500°C and pressures of 500 psi (3); years later some are still in everyday use. Three early models are shown in Figure 1. The actual diffusion membrane consists of a number of silver-palladium tubes, which are contained within the cylindrical cell.

Although the supply of diffusion cell components met the needs of a certain market it soon became apparent that this approach did not satisfy all demands and that there was a requirement for complete purification units. In response to this a series of small laboratory diffusion units were designed and manufactured. Since modified in design, such units still provide the purest form of hydrogen in a great many laboratories.

Fig. 1 From left to right, early model A71, A31 and A11 diffusion cells, the hydrogen outputs in standard cubic feet per hour were the same as their reference numbers. The cells were strongly made, and withstood pressures higher than were experienced in even abnormal usage. Pure hydrogen was provided from a single outlet at the far end of each cell. Much the same arrangement of silver-palladium tube membranes is in use in modern hydrogen diffusion equipment



To provide a considerably higher rate of hydrogen output (286 cubic metres of hydrogen per hour) a very few much larger diffusion units were built up from standard diffusion cells but the safeguards against contaminating impurities were less than adequate and these early units did not have satisfactory lifetimes.

The expansion of the electronics industry, which uses hydrogen during the manufacture of silicon chips, resulted in a rapid increase in the demand for hydrogen of a suitable quality. The hydrogen is used to carry doping elements onto the surface of the silicon wafer, and the gas must be of the highest purity. In this high technology industry a reliable supply of high purity gas is regarded as an essential everyday service, and new designs of palladium alloy diffusion units were required to satisfy this demand for hydrogen of near absolute purity. In practice it was found that a moisture meter installed in the gas stream served to monitor the purity of the hydrogen, and once in service dew points below −70°C are steadily recorded in diffusion units. Two typical purification units which use silver-palladium diffusion membranes are shown in Figure 2.

Many electronics factories are located long distances from traditional sources of commercial cylinder hydrogen, making them vulnerable to delivery delays caused by unusual weather or traffic conditions. A need for hydrogen self-sufficiency was recognised and led to the development of simple generators for on-site hydrogen production (4). These are fuelled by a methanol/water mixture which is cracked over a catalyst, the resulting hydrogen being extracted by diffusion through a palladium alloy membrane (5). The methanol/water mixture and its constituents are cheap and internationally available.

The use of this fuel effectively allows hydrogen to be stored as a liquid, moreover as a liquid which can be contained in thin walled vessels at atmospheric pressure, so providing a safer method of hydrogen storage than when the gas is kept under compression in high pressure cylinders.

The first methanol/water hydrogen generator

Fig. 2 Two HM2 diffusion units are shown here prior to despatch. In this range the units are supplied as two separate cabinets, one housing the gas purifying system and the other the electrical controls which therefore can be sited well away from the hydrogen gas system. These units provide a simple and economic means of upgrading commercially available hydrogen from a variety of gas sources to the ultra high purity required during the manufacture of semiconductor devices

Fig. 3 This containerised methanol/water hydrogen generator has been made for the British Antarctic Survey who will use the hydrogen to fill the balloons that lift sensitive meteorological instruments into the high atmosphere. The caboose is sledge mounted so that the whole self-contained unit can be moved regularly. It is hoped that this will prevent loss of the equipment by burial in heavy snowfalls and subsequent incorporation into the ice cap

Fig. 4 The G30 (Mark II) hydrogen generator installation at the E. I. Company Ltd., Shannon, Eire. The three G10 modules each show their vertical heat exchangers mounted behind a metal grid and small gas control panel. The units are housed in a building with louvered walls, visible here at the far end. The hydrogen is used in the manufacture of electronic products and for the production of television tubes. This was the most economic and reliable solution to the hydrogen requirements of E.I.

built by Johnson Matthey was successfully used in the Antarctic by the British Antarctic Survey, who in 1975 installed it in a simple shelter built out of its own packing case. This shelter is now buried deep in the Antarctic ice, under many years' accumulated snowfalls, and a third replacement unit has been supplied. The new G2 generator, capable of producing up to 2 cubic metres of hydrogen per hour at atmospheric pressure, is installed in one section of a

Fig. 5 A G40 (Mark I) generator installed at the Central Electricity Generating Board power station, Isle of Grain, Kent. The Dutch Barn shelter provides adequate protection for the four G10 modules. In the foreground are the methanol tanks which hold six months' supply of fuel. The yellow vertical pressure vessels are for storing hydrogen which is used for cooling the alternators. This application is a major outlet for methanol-fuelled hydrogen generators; the self-sufficiency they provide to remote power stations has already proved to be of especial value

caboose (Figure 3) where the electrical controls are also housed. However, the low pressure hydrogen store is located in an adjacent section. The whole caboose is sledge mounted and it is hoped that by frequently moving this around burial in the snow will be prevented.

Johnson Matthey Equipment

The steady growth in business based upon the palladium diffusion process led first to the formation of a small business group and more recently to the founding of a commercial company—Johnson Matthey Equipment Limited—whose main business is in on-site hydrogen generators. However, activities include the supply of small laboratory purification equipment with hydrogen outputs ranging from 28 litres per hour through to modules with outputs up to 56 cubic metres per hour. These may be linked together to form a much larger piece of purification equipment, but generally the modules are installed separately, just prior to the work station in order to reduce the risk of the pure gas becoming contaminated.

The development of on-site hydrogen generators has progressed from the first small units used to fill civil meteorological balloons to military units capable of producing 4.2 cubic metres per hour in almost any climatic condition. The market for civil on-site generators has grown steadily and many G10 units ($10m^3/h$) and a smaller number of the newer G25 units ($25m^3/h$) operate in industries as diverse as electronic device manufacture, alternator cooling in power stations, tungsten heat treatment, and in many others where merchant hydrogen has proved too expensive or where the supply is uncertain. Additionally a G50 module ($50m^3/h$) is to be introduced in the near future.

The commercial success of these generators depends largely upon their low operating costs, which enables hydrogen to be produced at a cost significantly below that of gas delivered in cylinders; this accounts for the short payback times for these generators. Compact size and near automatic operation are additional benefits while the purity of the hydrogen produced, at 99.9999 per cent, is a further bonus. Typical installations are shown in Figures 4 and 5.

Extending the Product Range

Following on the successful use of silver-palladium alloy for hydrogen production and purification, the manufacture of a range of equipment using a palladium on alumina catalyst has been started. This equipment removes oxygen from hydrogen gas streams that contain oxygen, or hydrogen from oxygen gas streams. The "Oxygone" range of equipment, as these units are called, represents a further broadening in the range of products offered by this new company, which is dedicated to the promotion of equipment utilising the remarkable physical and chemical properties of the platinum group metals.

References

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Hydrogen Storage for Vehicles

Hydrogen may be used as the fuel in suitable internal combustion engines and the possibility of using it to power motor vehicles is being considered. However, a major problem is that of storing the hydrogen in a compact, convenient form. A solution may be to use hydrogen to hydrogenate benzene to cyclohexane, which can be distributed in much the same way as petroleum products. The motorist would fill the tank of his vehicle with hydrogenated hydride, from which hydrogen would be released by an onboard catalytic dehydrogenation reactor.

Success could depend upon the dehydrogenation step, an endothermic reaction which is reversible. A report of a simulation study for a palladium on alumina catalyst indicates that a dehydrogenation reactor for cyclohexane is feasible, at least in theory (A. Touzani, D. Klvana and G. Bélanger, *Int. J. Hydrogen Energy*, 1984, **9**, (11), 929–936). Heat normally dissipated by the cooling system could be transferred to the reactor by a system of heat pipes, and would compensate for the endothermicity of the dehydrogenation reaction.