Thermal and Electrolytic Palladium Alloy Diffusion Cells

COMPLEMENTARY METHODS OF OBTAINING ULTRA-PURE HYDROGEN

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In this article the performance of thermal diffusion cells extracting pure hydrogen from mixed gas streams is discussed and the relationships between gas quality, output and extraction efficiency are summarised for convenience in the form of a graph applicable to any silver-palladium unit. Small quantities of ultra-pure hydrogen can also be generated by electrolytic diffusion, and the characteristics of a small prototype electrolytic cell are described and possible applications suggested.

Earlier articles in this journal (1, 2) have described the characteristics of a range of simple and effective diffusion cells which utilise a silver-palladium membrane permeable only to hydrogen. The primary object of these cells is to extract very pure hydrogen from a variety of gas mixtures. Although capable of producing ultra-pure hydrogen from any quality of feed gas, their output is largely dependent upon the proportion of hydrogen in the supply mixture. When this is great, high extraction efficiencies are possible; with poorer qualities of feed, high cell outputs can be achieved only at the expense of extraction efficiency. The extraction economics depend largely upon the balance between output and efficiency; this subject is considered below in a general manner.

The Extraction of Hydrogen from Mixed Gas Streams

The mixed gas stream fed to a diffusion cell is characterised by its total pressure and by its partial pressure of hydrogen. Some of the hydrogen fed into the cell diffuses through the palladium alloy membrane and emerges as a very pure gas. The remainder is carried out of the cell with the bleed and may possibly be returned to the main gas pipeline. The extraction efficiency depends upon the proportion of the total throughput of hydrogen which is usefully extracted.

The physical conditions within the cell are rather difficult to envisage, although it is not altogether unreasonable to interpret them diagrammatically as in Fig. 1. This shows a gas mixture containing a partial pressure of hydrogen P_1 being fed to a cell. At position A, where the partial pressure is still P_1 the diffusion rate is at a maximum. As the gas mixture moves along the tube nest it becomes progressively weaker in hydrogen, the partial pressure of which will have fallen to some value P_2 when the bleed valve has been reached. In the absence of accurate information about gas movement within the cell a detailed analysis is unjustifiable. Two extreme operating conditions can, however, be distinguished:

(1) The volume of gas bled off is so high that little change in composition occurs and the partial pressure of hydrogen within the cell remains constant at P_1.

(2) The volume of gas bled off is so small

that the partial pressure of hydrogen has fallen to zero before arrival at the bleed valve. This condition exists when the bleed rate is equal to the rate of arrival of gases other than hydrogen in the feed. If the bleed is reduced below this value, inert gases build up in the cell, the partial pressure of hydrogen falls to zero and diffusion ceases.

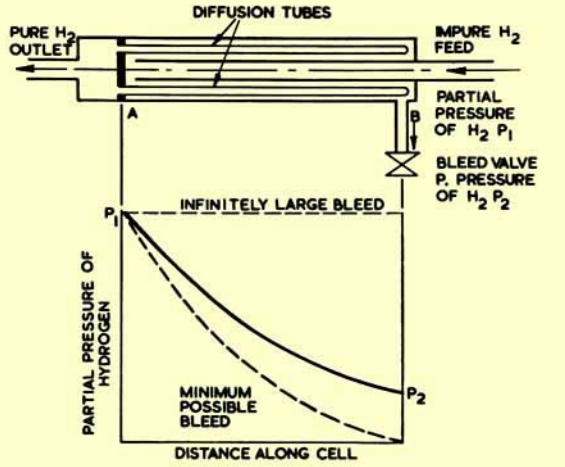

Fig. 1 Diagrammatic representation of the variation of hydrogen partial pressure within a diffusion cell

In the first instance the cell output is high although only a small proportion of the total throughput is extracted as pure hydrogen. In the second instance no hydrogen escapes through the bleed valve and the extraction efficiency is therefore 100 per cent. Because of the low partial pressure of hydrogen within the cell the output of hydrogen will be correspondingly low.

These relationships are conveniently expressed in graphical form in Fig. 2. This diagram illustrates the performance of any silver-palladium diffusion cell working at 400 p.s.i. at 400°C. The full thickness curves represent the output of pure hydrogen as a fraction of the maximum output attainable by feeding the cell on pure hydrogen.

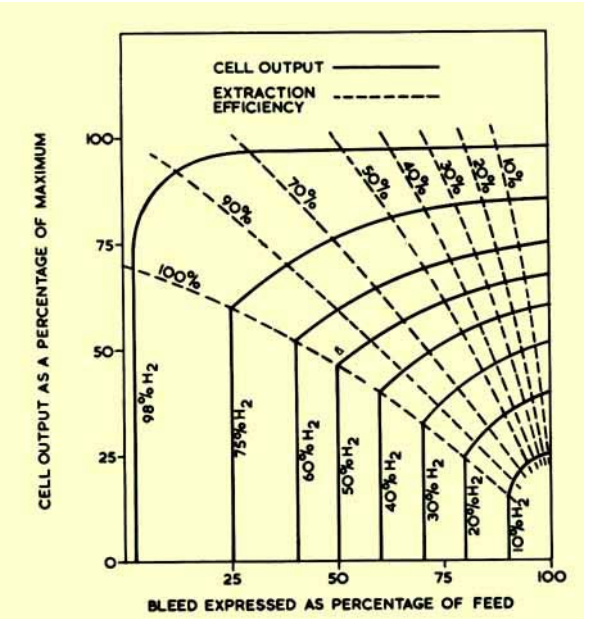

Fig. 2 Performance of a silver-palladium diffusion cell operated at 400°C and 400 p.s.i.

The cell might, for example, be fed with cracked ammonia at a total gas pressure of 400 p.s.i. This gas mixture contains 75 per cent of hydrogen. If half the gas feed to the cell were bled off, 65 per cent of the total hydrogen would be extracted and the cell output would be approximately 80 per cent of the theoretical maximum. Any significant reduction of bleed rate below 50 per cent would result in a rapid decrease of output. Although a 90 per cent extraction efficiency is possible with a 35 per cent bleed rate, the rapidly falling output curve indicates that unstable operation is likely within this region.

The diagram caters for gas mixtures containing 10 to 98 per cent of hydrogen. When the gas feed contains 98 per cent of hydrogen high extraction efficiencies are

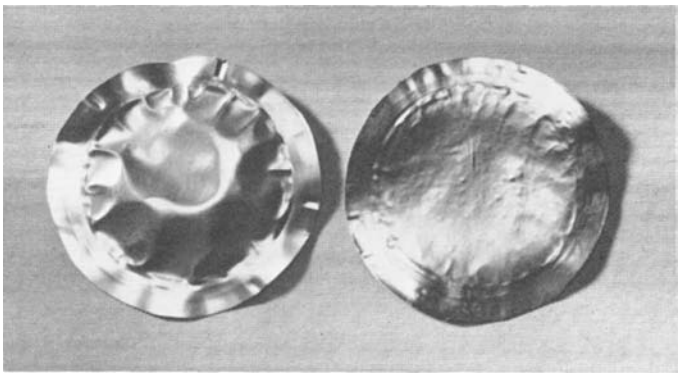

Fig. 3 Appearance of a pure palladium electrode (left) and a silver-palladium electrode after five cycles of charge and discharge

perfectly consistent with a high cell output and the extraction economics will not be significantly affected even if the bleed mixture is burned. Different considerations apply to a 50 per cent hydrogen mixture where economic considerations will usually require a return of the bleed gases to the process gas stream. Hydrogen has a high thermal capacity, and in plants of any size the heat from the pure hydrogen and bleed outlets must be used to preheat the gas feed by suitable interchangers.

The Electrolytic Transmission of Hydrogen through Silver-Palladium

It has been appreciated for many years that electrolytic hydrogen will diffuse through the walls of the tubular palladium cathode against which it is generated. This hitherto neglected possibility of simultaneous generation and purification has recently been utilised in the design of some compact electrolytic cells which can yield pure hydrogen for laboratory or other small scale work.

Some preliminary experiments on the electrolytic transmission of hydrogen through palladium were reported by Wahlin in 1951 and 1953 (3, 4). Hydrogen pressures of 700 p.s.i. were built up electrolytically, and it was shown that the diffused hydrogen was catalytically very active. It would, for example, react quantitatively with oxygen at room temperature and convert cyclohexene to cyclohexane. Recent work in these laboratories has shown that pure palladium is not an ideal cathode material for electrolytic cells. Better results are obtained with the 25 per cent silver-palladium alloy which expands less when fully charged with hydrogen (5). This effect is illustrated in Fig. 3, which compares the appearance of pure palladium and silver palladium electrodes each of which has been subjected to 5 cycles of charge and discharge at a current density of 0.2 amp per cm^2.

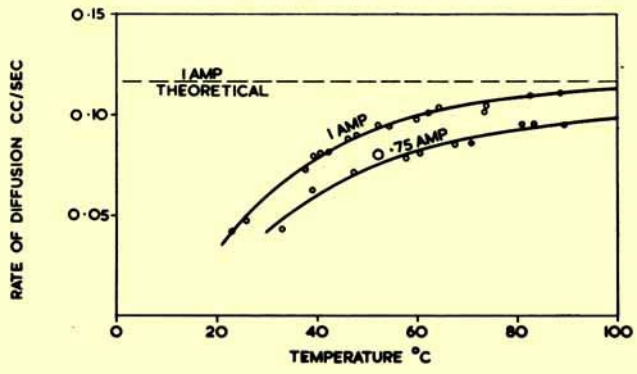

Fig. 4 Variation of transmission efficiency with temperature of a silver-palladium cathode working in a dilute sulphuric acid electrolyte

Electrolytic diffusion cells work best with a dilute sulphuric acid electrolyte. The electrode permeability increases with temperature, and the results shown in Fig. 4 indicate that transmission efficiencies of the order of 95 per cent can be attained at 80°C. Efficiencies of this order are compatible with current densities up to 0.3 amp per cm². The transmission efficiency does not decrease to any extent with increasing membrane thickness although it naturally takes longer for the hydrogen to permeate a thicker membrane. A time interval of six to seven minutes after switching on may elapse, for example, before hydrogen begins to leave the exit surface of a silver-palladium cathode 0.015 inch thick. Unless very high pressures are to be generated fairly thin cathodes can be employed and this time interval reduced to a minute or so.

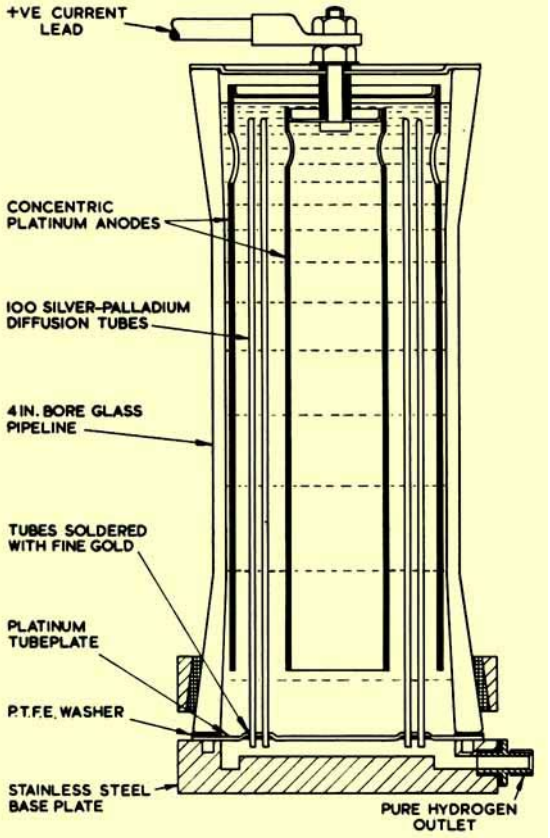

Fig. 5 Sectional view of a laboratory electrolytic diffusion cell

Fig. 5 provides a sectional view of a prototype cell which utilises for its cathode a multiplicity of closed ended silver-palladium tubes 0.063 inch outside diameter having a wall thickness of 0.003 inch. The unit is supplied with current from a small rectifier, and is capable of producing two litres per minute of hydrogen containing less than one part per million of impurities. The cell is self-heating, energy requirements being of the order of 500 watts for a pure hydrogen output of one litre per minute. A periodic addition of distilled water is the only attention required to ensure a continuous hydrogen output.

Sources of this type are obviously unsuitable for the economic generation of large quantities of pure hydrogen. They do, however, supplement the characteristics of the thermal diffusion cells and are likely to be usefully employed in laboratories where ultra-pure hydrogen is sometimes required but the total demand does not justify a high capital outlay. Electrolytic cells of the type described can work against outlet pressures of 400 p.s.i. and are conveniently used for supplying laboratory sintering furnaces with pure hydrogen, for gas chromatography and for hydrogenation experiments in organic chemistry.

References

1 J. B. Hunter, *Platinum Metals Rev.*, 1960, **4**, 130

2 H. Connor, *Platinum Metals Rev.*, 1962, **6**, 130

3 H. B. Wahlin, *J. Appl. Phys.*, 1951, **22**, 1503

4 H. B. Wahlin and V. O. Naumann, *J. Appl. Phys.*, 1953, **24**, 42

5 Johnson Matthey & Co Limited, British Patent Application No. 23343/62