Efficient Hydrogen Production with Palladium

Y.C. van Delft

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Yvonne van Delft, ECN

An increasing number of industries recognize the possible use of integrated reaction and advanced separation techniques to operate plants in an energy efficient and ecological way. It appears that hydrogen membrane reactors will have a very high potential. Palladium composite membranes for hydrogen separation have matured into such a state that demonstration in process industry and market introduction have been started.

Hydrogen is not only an important industrial chemical but is also seen as one of the future's key carbon free fuels. The 2003 world wide annual production of hydrogen was about 35 million tons with sales in excess of $2 billion in 2002. The amount of energy used for the production of hydrogen is substantial. The primary energy use is estimated to be 150 PJ, which is about 15% of energy consumption in the Dutch (petro) chemical industry. The availability of cheap natural gas and the relatively large proportion of refining, activities are the reason for this.

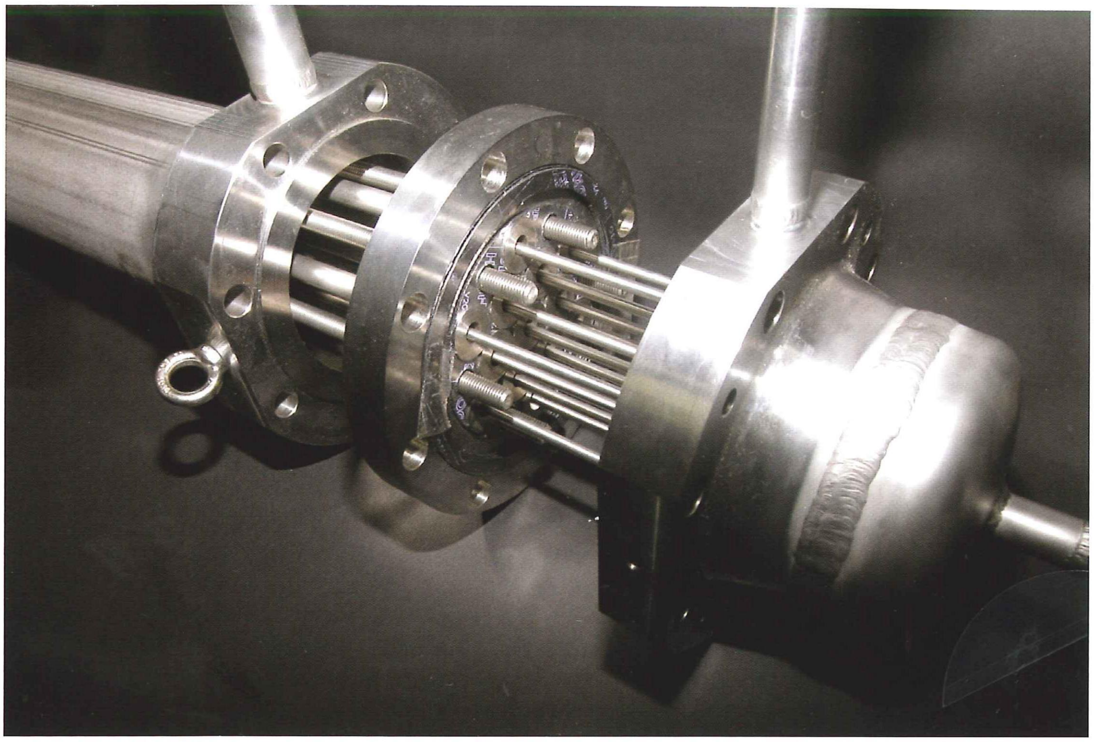
Hysep membrane module at the Tecnimont plant

The demand for hydrogen in petroleum refining will continue to increase due to the use of the cheaper heavy crude that contains more sulfur. Furthermore, the recent rapid development of more energy efficient fuel cells will substantially increase the hydrogen market. Therefore, the future demand for hydrogen will undoubtedly increase greatly. To lower the threshold to a future hydrogen economy, the current hydrogen production needs to become much more efficient. To realize this higher efficiency, an entirely new hydrogen production process with a lower cost, using much less energy and providing a higher quality product, has to be developed. All of this can be achieved by integrating hydrogen production and membrane separation.

The petrochemical industry produces industrial hydrogen at a large scale by a reaction that converts methane (natural gas) and steam into hydrogen and carbon monoxide. The gas that results from this process is called synthesis gas or syngas. The carbon monoxide is subsequently converted into carbon dioxide and hydrogen in the water/gas shift reaction. The entire reaction can be summarized in one formula, an equilibrium reaction:

$$CH_4 + 2\,H_2O \rightarrow 4\,H_2 + CO_2$$

In the industry these reactions take place at temperatures from 850 to 950°C and much heat loss occurs. The resulting CO_2 is separated from the hydrogen by means of absorption, which again involves major energy loss. To a large extent these losses can be avoided by combining



Hysep membrane module

suitable membranes with suitable catalysts in a membrane reactor, in which hydrogen production and gas separation take place in one reaction chamber. Palladium has been proven to let hydrogen pass through while blocking all other substances. If, during the reaction, the hydrogen is immediately separated with palladium membranes, the reaction equilibriums will shift to the right (production), making them more efficient and the reaction can take place at a much lower temperature (550 to 650 °C). The potential energy saving is therefore considerable. An extra advantage of the membrane reactor technology is its broad application. Since conversion of the raw material (natural gas) results in only two products; hydrogen and CO_2, the membrane reactor is both suitable for hydrogen production and CO_2 capture. Hydrogen membrane reactors are therefore a potential technology for the decarbonisation of fossil fuels and capturing of CO_2, which can be e.g stored in empty gas fields. However for this application the reactor will compete with other technologies for CO_2 separation.

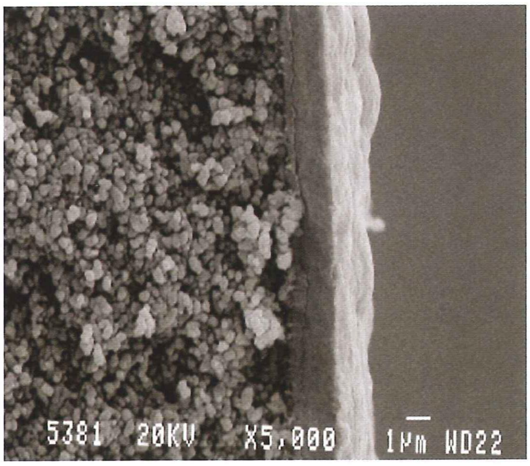
Low cost hydrogen separation

The most common types of Pd-based membranes are self-supporting metals foils with thicknesses of 25-100 µm. These membranes have the disadvantages that they are expensive with a low hydrogen flux. The performance can be improved if their thickness can be reduced. A thinner metal layer, however, has lower mechanical strength than a thick metallic membrane. In order to meet the challenge of attaining both high selectivity and good mechanical strength, metallic membranes have been deposited on strong supports.

The Energy Research Centre of the Netherlands (ECN) is capable of producing dense layers of Pd on a support tube as thin as 5 µm. Starting from a commercially available porous ceramic support tube, several intermediate layers are coated on the support with increasingly smaller pores. The thin palladium layer is applied on this tubular structure by electroless plating, because this procedure can be scaled up and industrialized and showed to be the most cost-effective technique. However, pure palladium under hydrogen (-containing) atmosphere goes through a phase change when it is cooled down from 450-550°C to room temperature. The temperature at which this phase change occurs can be changed by alloying the material with other metals, in particular silver. The process to produce a Pd alloy is sequential plating and annealing.

For sealing and joining the Pd alloy ceramic composite membranes to metal module end plates a graphite sealing technique has been developed and patented.

The state-of-the-art is illustrated by the fact that high selective Pd and PdAg membranes tubes are produced of a length up to 85 cm with a layer thickness of 3-9 µm. At this thickness the amount of palladium required (and therefore the cost) is low enough to enable commercial application and the membranes are among the world leaders in hydrogen flux. The main challenge, is to produce membranes with such a very thin Pd or Pd alloy layers, but having a reproducible performance and a long life-time.



SEM cross section of fractured sample of Pd membrane layer on ceramic support

Demonstration

The developed thin film Pd membranes are used to demonstrate the feasibility of energy efficient hydrogen membrane reactors. After achieving a spectacular methane conversion of more than 90% at a temperature of 550°C during a period of four weeks, ECN tested an installation with several membranes and a hydrogen production of approximately 1 Nm^3/h in 2009. A second generation membrane reactor with a hydrogen production of 5 Nm^3/h is now being build.

In the meantime the petrochemical industry has expressed its interest in the Pd membrane modules. In 2009, the world's largest module with thin film palladium membranes was delivered to Tecnimont KT for a hydrogen production test plant of 20 Nm^3/h. Several months of testing in an integrated plant in 2010 have shown both the feasibility of the innovative concept and excellent performance of ECN's Pd membrane technology. At the French company N-GHY the technology is tested for production of hydrogen for refueling cars locally from a variety of fuels, while capturing the CO_2 emitted in the process. In the GENSTOCK2 program N-GHY develops decentralized production units for production of pure hydrogen from biofuels, such as biogas, bioethanol, vegetables oils or esters. Next to the conversion of biofuels, the palladium based membranes are also used to convert coal into clean energy through hydrogen. CRL Energy from New Zealand carried out a unique experiment to demonstrate the full chain from coal to electricity. The institute used a Pd membrane module as a final step in converting coal gas to hydrogen with the purity required by the fuel cell. The project demonstrated that using this technology the whole chain, from coal to electricity, can be realized.

Commercialization

It will take a few more years to develop the membrane reactor into a commercial product. In order to pave the way for large-scale market introduction of membrane reactors, ECN wants to start up the production of a number of core components (such as palladium membranes). For this purpose an intermediate product will be commercialized: the Hysep modules. As these modules solely contain membranes, the Hysep modules are only suitable for hydrogen separation. They can be applied in recycling of hydrogen from, for example, waste flows from the production process of ammonia.
With the development of the membrane reactor and the Hysep modules an important milestone has been reached. Both the membrane reactor, with its multiple membrane tubes, and the Hysep modules have successfully passed their first test. The emergence of the initial market for the Hysep modules should lead to a collaboration with a commercial partner on scaling-up its production in the coming years. ■

Bron foto's: ECN