PGM HIGHLIGHTS

Palladium-Based Membranes for Hydrogen Separation

Introduction

For some years Italian groups have been at the forefront of research into membranes for hydrogen separation, with thin film palladium-based alloy membranes being a particular area of specialisation. The slower-than-predicted growth in the hydrogen economy has meant that the fruits of their research have yet to make a major impact in commercial terms but the quality of the research is well-recognised within the global membrane fraternity. Two recent books have been published (1, 2), which complement other recent chapters, reviews, presentations and articles, and highlight some of their work in the areas of membrane manufacture and utilisation within catalytic reactors, demanding applications in which marrying the performance requirements of the membranes with those of the catalysts has led many to suggest that neither technology is best served by the combination.

"Membrane Reactors for Hydrogen Production Processes"

This book (1) provides a consolidation of the results from a collaborative project, 'Hydrogen Production from Light Multi-Fuels and Storage in Porous Materials', started in 2006 by Italian academic and industrial groups to translate laboratory scale membrane reactors to pilot scale. Supported by the Italian Research Ministry under the Fondo Integrativo Speciale per la Ricerca (FISR) programme and managed by the University of L'Aquila, the success of the programme is demonstrated by the construction of a 20 $Nm^3 h^{-1}$ pilot plant at the Tecnimont KT SpA facility in Chieti Scalo, about 200 km north-east of Rome, in which pre-commercial membranes from four suppliers (ECN, MRT, Acktar and 'a Japanese company') were evaluated. Initially describing the general case for membrane reactors, for most of the book the authors have concentrated primarily on aspects of H_2 separation through dense Pd alloy membranes, with each chapter providing a stand-alone account of the topic it addresses.

The first chapter discusses the thermodynamic and kinetic aspects of the integration of selective membranes into chemical processes, utilising the ability to remove one of the product gases as a means of overcoming equilibrium constraints. The authors clearly lay out the equations governing the performance of membrane reactors, discussing formats in which the membrane is either in proximity with the catalyst or separated in order to optimise performance. Highlighting the enormous potential of membrane reactors, they acknowledge that commercial applications have been slow to be adopted, due in the main to a number of practical issues such as membrane stability, mass transfer limitations and high production costs.

These issues are ably discussed in Chapters 2 and 3, which cover the current 'state of the art' and economic requirements of small-scale Pd alloy membrane manufacture. Anyone who has worked in the area of H_2 separation will be aware of the rapid increase in publications associated with membrane fabrication and use in reactor systems. The lists of references for the two chapters, providing a good selection from groups around the world, bear testament to the large amount of money and time devoted to this area in the last two decades. Primary interest has been in thin film palladium-silver and palladium-copper alloy membranes, with as much time devoted to substrate preparation as to developing methods for forming the alloy foils to be supported. Most workers have concentrated on tubular geometries, as highlighted by three of the four suppliers to the programme. Only one, Membrane Reactor Technologies Ltd (MRT), from Canada, produces flat foil systems for these alloys, although this geometry has been more favoured by developers of the base metal alloy membranes. Notable absences among the membrane suppliers are some of the US groups, for example, Worcester Polytechnic Institute and Colorado School of Mines, who have long been fabricating systems capable of extended performance.

Integrated Modules and Reactor-Membrane Combinations

For the integrated membrane reactor modules, a large amount of work must go into the module design. To operate at maximum efficiency, the membrane must rapidly remove the product H_2 from the reaction zone. However, poor design can mean that, if the product H_2 is removed too quickly, its partial pressure in the reaction gas drops and segments of the membrane perform no function, adding needless cost to the module. Conversely, if the H_2 is removed too slowly, the desired equilibrium shift is not achieved. The additional requirements of the operational and maintenance aspects of the fully integrated membrane reactor, albeit having the advantage of in-reactor H_2 removal, mean that some workers have chosen to concentrate on staged membrane reactors, in which catalyst bed and gas separation functions are separated. Modelling of integrated and separated reactors is a critical function, highlighted in Chapter 4. With good membrane and catalyst performance data, coupled with algorithms capable of describing the radial and axial mixing, inter- and intra-particle diffusion and interfacial gradients between solid and fluid phases, modellers are able to accurately predict the performance of their membrane reactor designs.

Chapters 5–9 deal with the application of separation membranes to example chemical processes, either as integrated catalyst-membrane reactor units or as separated reactor–membrane combinations, offering the opportunity to run both at their optimum conditions. Chapter 5 looks at natural gas steam reforming (NGSR), modelling the performance benefits that could be obtained by switching from the traditional reactors to integrated membrane reactors. Whilst benefits can be found, the limitations imposed by forcing together two functions not running optimally lead the authors to the conclusion that separated reactor membrane combinations are necessary until membranes durable at NGSR conditions can be manufactured.

Autothermal Reforming and Water Gas Shift

Autothermal reforming (ATR) is considered in the next chapter. In this application, not only are the temperatures high but there are large thermal gradients present within the reactor. In the preamble, the authors point to references in which other groups have considered use of higher operating temperature ceramic membranes, both oxygen- and hydrogen-transporting versions, as means of improving efficiency of H_2 production. Within the study reported here, the group used a microporous alumina membrane (10 cm long × 1 cm diameter) with annular rings of foam-supported catalyst around the membrane. Reforming of methane was attempted, with some separation of the product H_2 observed. However, the authors rightly point out that, whilst this study shows encouraging results, there are many materials problems that need to be addressed before larger scale integrated ATR membrane reactors can be successfully constructed.

The water gas shift reaction is much more amenable to study within membrane reactors, due to its moderate temperatures, moderate exothermicity and pressure independence, meaning that operators can increase reactor pressures to drive separation membranes without adversely affecting conversion. Most investigators have constructed reactors based around either dense Pd or silica H_2 separation membranes, employed in different reactor-membrane configurations and with base metal and noble metal catalysts. The authors provide a good overview of the status of work at the time of writing, with a number of groups focusing upon the application within integrated gasification combined cycle (IGCC) power plants, where separation of H_2 from carbon dioxide streams would provide large commercial benefits. As with other candidate processes outlined in this book, workers are considering both integrated and staged reactor-membrane systems but the greatest gains are to be had with the integrated systems. In addition to managing the thermal issues, however, the coal-derived syngas will contain an array of contaminants that will rapidly poison Pd alloy membranes, with the result that workers must either develop efficient gas cleaning technologies or produce microporous membranes having high selectivity on a large scale.

Hydrogen Sulfide Cracking and Alkane Dehydrogenation

Membrane reactor enthusiasts are willing to trial many reactions in attempts to commercialise their technology, but few applications can be more demanding than the catalytic cracking of hydrogen sulfide. Having very limited industrial use, H_2S is generally viewed as a pollutant. Currently separated from hydrocarbon gas streams by amine adsorption, concentrated streams are treated by the barely economical Claus Process. However, the authors point out that, if H_2S could be decomposed to sulfur and hydrogen, this would yield valuable products that could offset the high costs associated with the decomposition process. Straightforward thermal decomposition requires temperatures well in excess of 1000ºC to achieve any level of commercial conversion and other potential decomposition technologies have not progressed beyond laboratory scale. Researchers have suggested, however, that the combination of two reactors separated by a microporous ceramic membrane unit could, with a great deal of process engineering, catalyst development and membrane scale-up, provide a commercial alternative for H_2S decomposition. To give an idea of the engineering requirement, the authors suggest that a 200 tonne/day plant would require a microporous membrane area of around 1800 m^2, somewhat beyond the fabrication capabilities of current manufacturers.

Alkane dehydrogenation reactions have been widely studied within membrane reactor modules, since removal of the formed H_2 should provide a useful product gas stream as well as conversions beyond those limited by equilibrium conditions. Chapter 9 begins with an overview of typical dehydrogenation processes, the catalysts used, typically alumina-supported chromium oxide and alumina-supported platinum, both with various promoters, and, more importantly, the drawbacks associated with the reactions. Thermodynamic restrictions, endothermicity, side reactions like cracking and isomerisation, rapid coke formation at excessive reaction temperatures and the need for low pressure operation are factors that combine to complicate the incorporation of dehydrogenation reactions into membrane reactors. Pd membranes have high selectivity, but their fragility means that many researchers have turned to the more durable microporous silica and zeolite membranes, although these are hampered by having low H_2 selectivities and generally show minimal impact upon the conversions achieved. The chapter gives an honest assessment of the status of membrane reactors for these processes, but points to some encouraging recent performance data suggesting that the technology may be developed in the future.

Pilot Plant and Commercialisation

The penultimate chapter discusses the design, successful construction and current status of the 20 $Nm^3 h^{-1}$ pilot plant at the Tecnimont KT SpA facility in Chieti Scalo, Italy (**Figure 1**), using natural gas steam reforming (SR) as the studied process. Design was based on the preliminary work described in Chapter 5. Typically, SR processes are run at 850–900ºC, too hot for incorporation of a Pd alloy membrane. Research has been carried out, using both base metal and platinum

Fig. 1. Membrane reforming reactor for hydrogen production (20 $Nm^3 h^{-1}$) in Chieti Scalo, Italy (Courtesy of Tecnimont KT SpA, Italy)

group metal (pgm) catalysts, to reduce the reaction temperature to 550–650ºC. However, this is still above the working temperatures for Pd alloy membranes, so the pilot plant was constructed with two paired reformers and membrane separation units in series. Pre-commercial membrane modules were obtained from the four suppliers. Three modules incorporated tubular membranes, whilst the MRT unit was fitted with flat-sheet membranes.

Feeding desulfurised natural gas into the process, the operational parameters of the reformers were characterised in order to control the feedgas to the membrane units. The results presented are those from the first preliminary experiments. That the membranes are having an effect is clear, but the conclusions section makes the claim that 'four types of Pd-based H_2 selective membranes are tested and compared', which is perhaps slightly misleading. No comparative data is shown for the membrane modules and only limited performance data for two of them. More testing was planned at the time of writing, so better assessment of the modules should now be possible.

The final chapter draws together the key points from the previous chapters and examines the prospects for membrane reactors, forecasting a very positive future for the Pd systems. Clearly, there are several key obstacles to their widespread use:

- fabrication costs, although this is less the cost of the Pd and more the labour intensive routes to produce the membranes;
- membrane stability under poisoning and process conditions, necessitating the use of staged reactors for some processes;
- a current lack of industry-produced, commercial scale units;
- no acceptable accelerated ageing tests, without which longevity can only be assessed by actually carrying out thousands of hours of testing.

However, the authors cite the recent advances in substrate development, Pd layer deposition, module modelling and design and the beneficial efficiencies that successful commercialisation would bring as demonstrating the need for development to continue.

Overall, the book provides a very good summary of both the field of Pd membrane reactors and, specifically, the recent work carried out by primarily European groups, culminating in the successful construction and operation of the pilot plant in Chieti Scalo. The reviewer may not quite share the long-term optimism of the authors but their commitment is undeniable and progress to date has been impressive. We await future developments with great interest.

"Preparation of Thin Film Pd Membranes for H_2 Separation from Synthesis Gas and Detailed Design of a Permeability Testing Unit"

The experience of the Italian research groups is further highlighted by the second book (2), predating the first and concentrating on the manufacture and testing of Pd-only membranes on porous steel supports by the group at the University of Pisa. This study was also financed (in part) by the Italian Research Ministry under the FISR programme.

Constructed in the format of a doctoral thesis or extended journal publication, the 74-page book begins with a discussion around the overall area of H_2 generation and subsequent applications, before highlighting various membrane types available for gas separation: dense metallic and ceramic, polymeric, microporous ceramic and composite.

The second chapter summarises the specific properties that give rise to the use of Pd membranes and some of the methods used to fabricate the thin-walled, supported films desirable for large-scale, cost-efficient separation. As with other membrane reviews in recent years, the authors highlight the large number of journal articles and patents associated with Pd membrane development. The reader, and probably several funding bodies, may be left to ponder just how much more work and how many more research dollars will be needed before the technology is viable for long-term, large-scale operation.

Manufacture of Thin Palladium Films

The manufacturing route and equipment used for the thin Pd films on discs and tubes – cleaning, surface oxidation, preactivation and electroless plating – is similar to that used by other groups, for example, Ma's group at the Worcester Polytechnic Institute, USA. Many groups have now moved beyond the simple oxidation of the steel surface to incorporate a diffusion barrier, such as alumina or nitrides, to minimise the risk of Pd migration into the steel substrate. Observations during the preparation are noted in Chapter 4 and here the reviewer must applaud the authors. Too often authors gloss over the minor experimental details, leaving out key points which may seem obvious at the time. Whilst everyone appreciates the importance of 'trade secrets', the time may be approaching when funding will begin to decline if the promised growth in commercial applications fails to materialise, and sharing 'minor' details among the membrane community may go some way to minimise wasted time.

Membrane thicknesses of between 10–17 μm were produced, with higher plating efficiencies noted for the disc-based membranes. This was reasonably ascribed to loss of Pd by plating out on the walls of the recirculating equipment used for the tubular versions. Leak testing of tubular membranes at ambient temperature, using nitrogen pressurisation testing and immersion in water for bubble formation, showed that, unsurprisingly, leaks decreased with Pd thickness. The principal area for leaks to occur was around the welded join between the porous steel support and the dense end attached for sealing, suggesting that further work is required to avoid irregular Pd deposition and delamination in that area. For the future, the authors might consider leak testing with helium, which will pinpoint holes more readily than nitrogen.

The experimental setup for testing the H_2 separation capabilities of the membranes, described in Chapter 5, is quite thorough. It includes not only the usual capability to test in pure H_2 and model syngas streams, but also can introduce poisons such as sulfur, ammonia and hydrocarbons. Frustratingly, the book ends without test data being presented and no indication of when or where such data may be found, requiring the interested reader to search the usual literature sources. Although the title specifies the preparation and design aspects, it is unclear why the book was published without giving the reader a flavour of the membrane performance under application conditions.

A search did uncover some details of testing carried out on a range of tubular membranes, having a surface area of 19 cm^2, supported on porous stainless steel supports and prepared by varying deposition parameters (3). Testing at elevated temperatures and pressures was carried out in pure H_2, N_2 and CO_2, with the H_2 selectivity being calculated and no deterioration seen over 500 hours of testing. The permeation data was subsequently used to model the performance of a 3 m long membrane having 50% H_2:50% CO_2 feedgas. Despite having the gases available, it appears that they did not use that mixed feedgas during their experimental campaign, which would have supported their calculated selectivities and modelling results. Perhaps that information will form the basis of new reports.

Conclusion

Looking at the details of the FISR programme, it is clear that the Italian government is committed to investing in a hydrogen capability and infrastructure and in renewable energy sources. The construction of the Chieti Scalo plant shows that the years of experience in laboratory-scale membranes and reactors can be translated to pilot-scale, with encouraging early results. Membrane researchers worldwide will look forward to future developments.

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References

1 "Membrane Reactors for Hydrogen Production Processes", eds. M. De Falco, L. Marrelli and G. Iaquaniello, Springer-Verlag, London, UK, 2011

2 M. Bientinesi and L. Petarca, "Preparation of Thin Film Pd Membranes for H_2 Separation from Synthesis Gas and Detailed Design of a Permeability Testing Unit", Nova Science Publishers, Inc, New York, USA, 2010

3 M. Bientinesi and L. Petarca, *Chem. Eng. Trans.*, 2011, **24**, 763

The Reviewer

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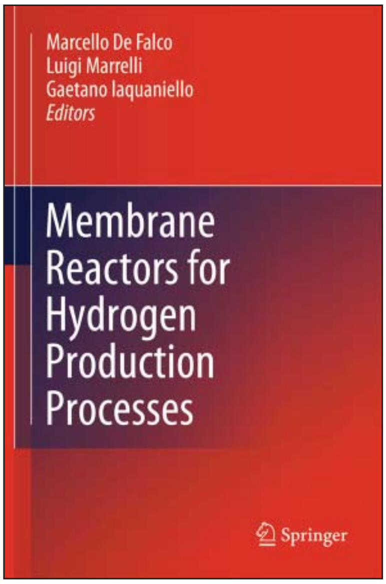

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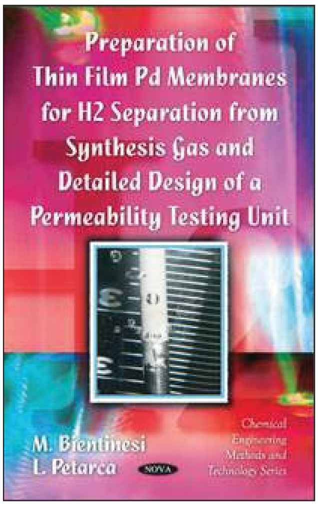

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