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"Palladium Membrane Technology for Hydrogen Production, Carbon Capture and Other Applications"

Edited by Aggelos Doukelis (National Technical University of Athens, Greece), Kyriakos Panopoulos (Chemical Process and Energy Resources Institute, Greece), Antonios Koumanakos and Emmanouil Kakaras (National Technical University of Athens, Greece), Woodhead Publishing, an imprint of Elsevier, Cambridge, UK, 2015, 383 pages, ISBN: 978-1-78242-234-1, £170.00, US$280.00

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1. Introduction

The European Union (EU) has invested heavily in palladium membrane technology, as reflected by numerous multi-million Euro research projects funded over the last decades. As a result, many research groups in Europe, both from academia and research institutes, have been leading the development of Pd membrane technology targeting hydrogen production, carbon capture and other important industrial applications. However, much of this research has yet to make a major impact commercially, mainly due to the slowdown in global economic growth in recent years which, in turn, has slowed the adoption of the hydrogen economy. This book complements another recent book (1), with this one covering in greater detail the challenges in manufacturing Pd membranes and focuses on using Pd membranes in different H_2 manufacturing processes. In contrast, the earlier book concentrated on a wider range of potential applications for Pd membranes but the discussion on membrane manufacturing was more limited. The earlier book (1) has also been reviewed in this journal (2).

The chapters from the present book feature contributions from the participants in several multi-million Euro collaborative research projects and also from Tokyo Gas, Japan. This book collects many of the advancements in Pd membrane technology made within the EU, covering both fundamental and applied aspects. The book is divided into two parts, namely: (a) Pd membrane fabrication and reactor design (Chapters 2 to 9) and (b) potential application of Pd membranes in industrial processes (Chapters 10 to 16).

Chapter 1, by K. Atsonios (National Technical University of Athens and Centre for Research and Technology Hellas, Greece) *et al.*, gives a very good overview on the current status of Pd membrane technology. It begins with a comparison between Pd membranes and other H_2 permselective membranes in terms of their operating characteristics and separation mechanisms. The authors then explain the different benefits brought about by alloying Pd membranes and also the past and current research trends in alloying. The manufacturing of Pd membranes is briefly covered by examining the different methods of depositing the dense Pd layer, the support characteristics required and the advantages and disadvantages of using different supports. The chapter then concludes by introducing the potential benefits of using Pd membranes in electricity production and carbon capture, in the H_2 economy for pure H_2 production and the chemical industry for chemical upgrading.

2. Palladium Membrane Fabrication

2.1 Fabricating the Dense Palladium Layer

The various methods of fabricating the dense Pd layers, such as magnetron sputtering, electroplating and self-supporting Pd membranes, are covered more in-depth in Chapters 2, 3, 5 and 6. Chapter 2 by T. A. Peters, M. Strange and R. Bredesen (SINTEF Materials and Chemistry, Norway) discusses the two-stage physical vapour deposition (PVD) Pd membrane fabrication method developed at SINTEF. Essentially this method involves: (a) depositing a thin layer of Pd or Pd alloy onto a polished silicon crystal substrate and (b) manually removing the dense Pd or Pd alloy layer from the substrate, with the dense layer subsequently integrated onto a support or module. Numerous examples in this chapter illustrate the flexibility of the two-stage PVD fabrication method where various binary and ternary Pd alloy compositions were investigated. Examples in Chapter 2 also show the integration of Pd membranes into micro-channel systems which is only possible when the membrane is fabricated by PVD.

Another important and very popular method to fabricate Pd membranes is electroless plating and this is reviewed in Chapter 3 by M. J. den Exter (Energy Research Centre of the Netherlands (ECN), The Netherlands). The Hysep® pre-commercial Pd membranes were developed and are offered by ECN. These membranes are synthesised by electroless plating. The chapter begins with the chemistry behind this process followed by an overview of electroless plating of various metals for other applications. The authors then present various thin film deposition technologies and consider whether each method will be suitable for fabricating Pd membranes. The chapter then concludes with ECN's experience in upscaling electroless plating to manufacture Pd membranes and the possible pitfalls are deliberated.

Pore-fill Pd membrane fabrication, which was developed by, among others, Tecnalia Research and Innovation, Spain, is a variation of electroless plating and is scrutinised in Chapter 5 by D. A. Pacheco Tanaka (Tecnalia Research and Innovation), J. Okazaki (JGC Corporation, Japan), M. A. Llosa Tanco (University of Porto, Portugal) and T. M. Suzuki (National Institute of Advanced Industrial Science and Technology (AIST), Japan). Pore-fill Pd membrane fabrication is a four step process which involves: (a) coating the support with a nanoporous ceramic layer; (b) seeding where Pd particles are deposited on the porous ceramic; (c) coating the protective layer and (d) electroless plating where a dense Pd layer is deposited on the porous ceramic layer. The authors suggest that this membrane exhibits better mechanical stability as the dense Pd layer is not exposed on the surface. They illustrate an example of the pore-fill Pd membranes exhibiting higher H_2 permeance compared to other Pd membranes, thereby illustrating the need for a thinner Pd layer with improved mechanical durability. This chapter concludes by showing that the choice of support is an important factor in determining the stability of Pd membranes.

The manufacturing of self-supported palladium-silver membranes is comprehensively described in Chapter 6 by S. Tosti (Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Italy). The physical properties of Pd-Ag alloy are discussed and the author takes a theoretical approach to show the compromise in durability and selectivity when using a supported Pd membrane. The kinetic and thermodynamic expressions for H_2 transport through Pd membranes are presented, and the ways in which these follow and deviate from Sieverts' law are analysed. The use of cold-rolling and diffusion welding to produce thin walled Pd-Ag membranes is then discussed. The module designs for the dense Pd-Ag membranes are investigated and ENEA's dense Pd-Ag membranes for producing ultra-pure H_2 *via* dehydrogenation, water gas shift and reforming reactions are demonstrated in a laboratory-scale unit. The dense membranes are also shown to be useful for recovery of H_2 isotopes in the fusion reactor fuel cycle.

Although Chapters 2, 3, 5 and 6 give a very good background on the fundamentals and applications of different methods to fabricate Pd membranes, there is very little synergy and links between these chapters where the different methods are evaluated against each other. The explanation of the potential difficulties of each method is rather limited.

2.2 Support Fabrication for Composite Palladium Membranes

Composite or supported Pd membranes are by far the most widely investigated type, especially for industrial applications, due to the need to decrease the thickness of the Pd layer, for both performance and economic reasons, and also to increase the mechanical strength of the membrane in order to withstand the applied differential pressures. Chapter 4 by H. Richter (Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), Germany, features the fabrication of ceramic substrates to use as supports in Pd membranes. One of the advantages of using a ceramic substrate is the ability to tailor its pore size to suit the method by which the dense Pd layer is fabricated. The method to tailor the pore size of the ceramic substrate builds upon the vast experience of preparing ceramic membranes for microfiltration (MF) and ultrafiltration (UF). The author gives a general introduction to the fabrication of tubular and flat ceramic substrates for MF. However, ceramic MF membranes are not directly suitable as supports for the deposition of the dense Pd layer due to their large surface pore sizes. Ceramic MF membranes will require post-synthesis modification *via* coating or sol-gel to make UF membranes. The details for these post-synthesis modifications are reported in this chapter. Although similar, the ceramic UF membranes used for liquid filtration may also not be satisfactory as direct supports for Pd membranes. The additional requirements to use UF ceramic membranes as supports for Pd membranes are examined. Finally, the chapter concludes by considering the opportunities of decreasing the cost of ceramic membranes.

This chapter gives a very good overview on the technology behind making ceramic supports used for manufacturing Pd membranes. However, due to the brittle nature of ceramic supports, many large scale industrial applications would prefer more robust stainless steel supports for Pd membranes. The reader would gain a better appreciation of the supports if a chapter on stainless steel supports were also included.

2.3 Pilot Scale Membrane Testing

Chapter 7 by G. Iaquaniello, E. Palo (Kinetics Technology (KT) SpA, Italy), A. Salladini and B. Cucchiella (Processi Innovativi Srl, Italy), shares the authors' experience of testing Pd membrane modules in their membrane-assisted steam methane reforming pilot plant, some details of which were presented in the earlier book (2). This pilot plant is based on an open architecture, where a reformer and a membrane unit are connected in series to form a reformer and membrane module (RMM). The number of modules can be increased to achieve the desired performance. The purpose of this pilot plant is to investigate the feasibility of implementing such a system at industrial scale and to study the membrane performance and stability. KT provided the details on the specification of their RMM pilot plant and the different modes of operation tested. After briefly summarising the differences of the pre-commercial Pd membranes from three different suppliers, namely ECN (The Netherlands), NGK (Japan) and MRT (Canada), the performances and relative merits of these membranes were compared against one another.

2.4 Modelling Palladium Membrane Reactors

Chapters 8 and 9 explain the use of modelling to design an integrated Pd membrane reactor. The modelling of steam methane reforming and of propane dehydrogenation for both a packed bed membrane reactor (PBMR) and a RMM were analysed in Chapter 8 by M. Sheintuch (Technion – Israel Institute of Technology). There is a general discussion on the parameters which are essential in a membrane reactor design. Equations were derived to relate the H_2 removal rate (H_2 permeance through a membrane) to the rate of reaction assuming that only a single reaction is taking place. The equation was then used to estimate the required membrane area from the required conversion. Similar equations were derived for RMM, where the required membrane area and number of stages can be predicted. Building on these basic models, further parameters were included taking into account side reactions and the supply of heat from both adiabatic systems and heated systems. The modelling results for propane dehydrogenation are reviewed.

Chapter 9 by J. C. Morud (SINTEF Materials and Chemistry) examines in detail the building of the model to describe a single-tube reactor design (a membrane is placed within an outer tube). The model is then programmed in FORmula TRANslation (FORTRAN) and made callable using Excel. Based on user input data, the simulator can be used for sizing the reactors or separators while simultaneously assessing the mass transfer, pressure drop and membrane area. The model consists of mass and energy balance, reactions and discretisation to account for the radial direction. Sub-models are then included to account for the fluid flow field, membrane fluxes, reaction kinetics and pressure drop calculations. This chapter concludes by discussing the use of this single-tube model as an approximation for a multi-tube design.

Both chapters gave a very good overview on the approach and assumptions to derive models to simulate Pd membrane reactors or separators. The models derived in Chapter 9 are more rigorous than the approach used in Chapter 8. Chapter 8 gives clear examples on the information which can be attained from the models; however, the reviewers would have liked to have seen a short example included from the more rigorous modelling in Chapter 9.

3. Palladium Membranes in Reactors: Designs and Applications

3.1 Palladium Membranes in Steam Reforming

Pd membranes have been proposed to be combined with steam reforming to remove H_2 from the reactor, thereby driving the reaction forward at lower temperature with a reasonable conversion. Chapters 10, 13, 14 and 15 describe the use of Pd membranes in steam reforming.

A novel concept of using solar energy as a heat source for steam reforming is presented in Chapter 10 by A. Giaconia (ENEA Research Centre). By using molten salts as the heat carrier in a concentrating solar power (CSP) plant, energy is supplied to drive the reaction. However, these molten salts can only be heated to 600ºC, so the Pd membrane must be used to recover the H_2 to increase the conversion at lower temperatures. A comparison between an integrated and non-integrated reactor-membrane system in a solar powered steam reforming unit is included.

The experience KT gained in studying a 20 $Nm^3\ h^{-1}\ H_2$ capacity RMM pilot plant is outlined in Chapter 13 by G. Iaquaniello, E. Palo, A. Salladini and B. Cucchiella. The chapter, which again builds on the material in the earlier book (2), begins with a brief description of the pilot plant and its different operating modes. The pilot plant was used to gather relevant data and issues related to the operation of the RMM on an industrial scale. The influence of the reformer temperature and membrane area on the methane conversion was discussed. Based on the data collected, the number of RMM required to achieve different conversion was also estimated. The results indicated the reliability of a semi-industrial scale RMM and the flexibility of operating a non-integrated reactor-membrane system.

The development route which enabled Tokyo Gas to study a 40 $Nm^3\ h^{-1}\ H_2$ capacity integrated membrane reformer is described in Chapter 14. A brief synopsis of the membrane-reformer system is given with details on the thickness of the Pd membrane, number of membranes in each module and the arrangement of the modules into the reactor system. Tokyo Gas first evaluated the membrane reformer with and without carbon dioxide capture before proceeding to demonstrate the long-term durability of a single membrane reformer module. The failure of their first test after 3000 hours due to serious leaks has led to the progression of an improved membrane module which was shown to be stable for over 13,000 hours of continuous operation, forming the basis for the development of the 40 $Nm^3\ h^{-1}$ reformer-membrane system. In order to reduce cost of the system, Tokyo Gas and NGK are currently developing a membrane-on-catalyst (MOC) module which is claimed to exhibit higher performance at a lower cost.

Chapter 15 by F. Gallucci, M. van Sint Annaland (Eindhoven University of Technology, The Netherlands), L. Roses (HyGear BV, The Netherlands) and G. Manzolini (Politecnico di Milano, Italy) looks at the possible use of Pd membrane reactors in micro-combined heat and power (m-CHP) applications. This chapter briefly outlines the development of m-CHP followed by a general comparison between packed bed and fluidised bed membrane reactors, and the differences between these membrane reactors used in m-CHP in terms of efficiency and energy losses are studied.

3.2 Palladium Membranes in Combined Cycle Power Plant

The use of Pd membranes in integrated gasification combined cycle (IGCC) and natural gas combined cycle (NGCC) power plants is discussed respectively in Chapter 11 by M. Gazzani (Eidgenössische Technische Hochschule (ETH) Zurich, Switzerland) and G. Manzolini and in Chapter 12 by K. Atsonios *et al.* In both chapters, which are quite thorough in their overviews, Pd membranes were used as separate units instead of an integrated Pd membrane reactor. This decision was based on techno-economic evaluations and on operability studies. Both chapters are presented in a very similar way; an overview is given on the IGCC or

NGCC power plant, followed by a discussion of the operating parameters of the power plant performance and finally the techno-economic evaluation is examined. However, the focus of the explanation in both chapters is very different.

Chapter 11 is dedicated to the requirements of the Pd membrane in an IGCC power plant and contains an in-depth analysis of its design and concepts. A very good introduction is given to existing sulfur removal technologies and how they can be accommodated with Pd membrane systems, which are notoriously susceptible to surface poisoning, and future sulfur removal technologies which are in development.

Chapter 12 explores the NGCC plant in depth and contains a detailed techno-economic analysis with case studies. However, the different options of using Pd membrane in a NGCC plant and its implications are, perhaps, not as well covered, although the conclusion that the application will be driven only by proven membrane stability and robustness is common with all other areas.

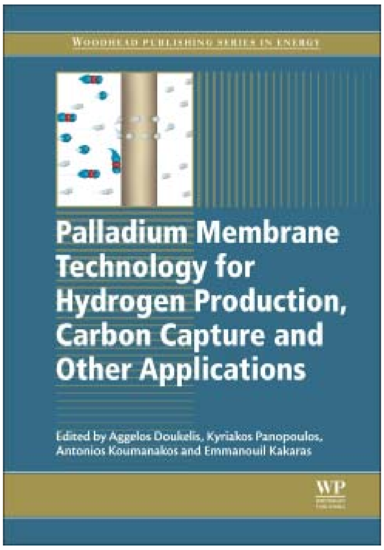
3.3 Palladium Membranes in Speculative Applications

Over the years Pd membranes have been investigated in numerous applications where H_2 is involved and a selection of these are reported in Chapter 16 by K. Atsonios *et al.* The key advantages of using Pd membranes in areas such as separation, H_2 production, chemicals production, fuel upgrading and waste water treatment are briefly summarised. This chapter would have been beneficial to the reader if the potential drawbacks or problems of using Pd membranes in the above mentioned areas were more clearly highlighted. Some of the applications discussed were only investigated in modelling but not demonstrated experimentally. It would have been clearer if the authors distinguished between these.

4. Conclusion

Overall this book provides a very good overview on the recent development of Pd membranes mainly in the EU. It covers both the fabrication of Pd membranes and their potential utilisation in numerous applications. Each chapter gives a brief introduction to the fundamental aspects of Pd membranes before a further in-depth discussion commences. Most chapters assess the potential benefits of using Pd membranes in different applications. It would have been helpful to the reader if the potential pitfalls and technology gaps in applying Pd membranes were addressed in greater detail.

Researchers in Pd membranes will be familiar with various sections of the book, since portions have appeared in other texts and publications. Nevertheless, the breadth and depth of the Pd membrane technology advances are well covered in this book, which makes it a suitable reference for people who are looking for a good introduction to Pd membranes and also for experts in this field who are looking for a good 'all-in-one-place' overview.



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The Reviewers

Xavier (Xian-Yang) Quek graduated with a BEng in Chemical Engineering from Nanyang Technological University, Singapore, and a PhD in heterogeneous catalysis from Eindhoven University of Technology, the Netherlands. In 2013, he joined the Low Carbon Technology group at Johnson Matthey Technology Centre, Sonning Common, UK. His research focused on the use of palladium and palladium alloy membranes for pre-combustion carbon capture. He also has a wider interest in membranes and the use of membranes in various processes. He left Johnson Matthey in April 2016.

Hugh Hamilton has worked at the Johnson Matthey Technology Centre, Sonning Common, UK, for nearly 28 years, during which time he has researched in a range of areas including autocatalysts, palladium membranes, fuel cell membrane electrode assembly manufacture, hydrogen storage, titanium powder metallurgy, sorbent development for removing mercury from syngas and modified atmosphere packaging. His current role includes reviewing technologies in areas of interest to Johnson Matthey and various external collaborations around materials development.

