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"Nonporous Inorganic Membranes: for Chemical Processing"

EDITED BY ANTHONY F. SAMMELLS AND MICHAEL V. MUNDSCHAU (Eltron Research Inc, U.S.A.), Wiley-VCH, Weinheim, Germany, 2006, 291 pages, ISBN 978-3-527-31342-6, £80.00, €120.00

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Amid the current global preoccupation with the lightest element as a means to alleviate the consequences of the dwindling supplies of fossil fuels, this book sets out to provide an overview of the area of dense oxygen and hydrogen transport membranes and the roles they could play within technologies being developed to improve on the poor efficiencies associated with simple combustion processes. The book's editors, themselves long-time practitioners in the field of dense membrane research, have assembled a group of authors whose names will be familiar to researchers in the area.

Membrane Applications of the Platinum Group Metals

Application of the platinum group metals (PGMs) within the area of fully dense membranes falls into three categories:

- The entire membrane may be fabricated from a PGM or PGM-based alloy, as in the case of hydrogen transport membranes fabricated from Pd and alloys thereof.
- The PGM phase can be added to a ceramic oxide phase to form a 'cermet' material.
- Thin PGM coatings may be deposited upon the surface of fully dense materials to improve dissociation/association kinetics, act as protective coatings or as electrode materials in driven membrane systems.

Each of these areas is discussed, in varying lengths, within the context of the various chapters.

The first two chapters cover the area of hydrogen-permeable, dense, ceramic materials with mixed protonic-electronic conductivity that are based almost exclusively upon oxides. Of specific interest to the PGM industry are the sections dealing with the cermet materials, where pairing of oxides with metals (typically 10 to 40 vol.% of palladium, platinum, palladium alloys or refractory metals such as tantalum or niobium etc.) allows researchers to circumvent potential problems relating to having both conduction types in a single phase. The practical *caveat* with these materials is their poor mechanical stability, primarily due to internal interfacial stresses.

In a reference-laden Chapter 3, Stephen N. Paglieri (Los Alamos National Laboratory, U.S.A.) amply highlights the huge effort that has been devoted to fabricating thin palladium-based hydrogen diffusion membranes. 'Thick' membranes, capable of achieving ultra-high purity hydrogen, have been available for over thirty years, but these are prohibitively expensive for applications that require only moderate purity levels. The author provides a concise overview of the areas that must be addressed in order to produce a viable thin membrane – the nature of the support, deposition and/or alloying techniques for the active layer, the effects and mitigation of poisons, the difficulties surrounding sealing of the membranes into housings, and of course the final cost implications. It is a measure of the dedication of the membrane industry and funding bodies that so much funding has been made available in the quest for what remains an elusive product.

The metallic competition to Pd systems is described in Chapter 4 by Michael V. Mundschau, Xiaobing Xie and Carl R. Evenson (Eltron Research Inc). The so-called 'superpermeable' membranes, based upon niobium, tantalum and vanadium, were developed for the nuclear industry to separate hydrogen isotopes from helium in plasmas and from molten metal cooling fluids. The burgeoning interest in the hydrogen economy and the high cost of Pd have reinvigorated research in these alloys as an alternative for hydrogen purification in the chemical and energy industries. However, these metals are very prone to formation of surface oxides, carbides and nitrides that poison the hydrogen dissociation reaction. This leads developers to coat the surfaces with PGM layers which in part protect the surface from poisoning and facilitate hydrogen ingress into the membrane beneath. The importance of matching the expansion properties of the catalyst layer with the membrane and the criticality of the deposition method are highlighted, but the authors clearly believe that these membrane systems will provide a commercially viable industrial membrane.

The down-to-earth comments by David J. Edlund at the start of Chapter 5 remind us that, without a suitable module, a membrane is merely a laboratory curiosity. Of the myriad groups developing new membrane compositions only a few are concurrently engineering new modules, which fall into two designs – those that will accommodate foils and those for tubular membranes. 'Thick' palladium-silver alloy membrane systems, such as those available from Johnson Matthey (1), tend to be tubular in form, primarily because during the 1960s when they were developed, sealing of foils was problematic. Nevertheless, a huge amount of work on brazing alloys was necessary before commercial systems were suitably reliable. Subsequent development of palladium-copper alloy foil has allowed modules based around stacks of foils to be constructed successfully for commercial applications. This excellent chapter provides the engineering viewpoint that is often neglected by membrane developers.

The following three chapters cover the area of oxygen transport membranes which, although fascinating materials with great possibilities, have only very limited opportunities for PGM usage. Early researchers doped oxide materials with Pd or Pt to form 'dual phase' structures in which the dopant introduced electronic conductivity. However, cost and long-term mechanical instability resulted in cessation of this practice. The PGMs have also been introduced onto the membrane surface to act as catalysts. For example, "significant improvements" in ethene yields and selectivities were noted when dispersed Pd was introduced onto the membrane for alkane dehydrogenation reactions.

The book finishes with discussion of the economics of membrane reactors using the water gas shift reaction over a Pd membrane as a case study. In agreement with the comments by Edlund in Chapter 5, the author notes that, although the potential of membrane reactors has been widely acclaimed, the technology has yet to proceed beyond laboratory scale. There are several technical barriers to be overcome, including sealing, thermal cyclability, high temperatures and pressures in aggressive environments, catalyst and membrane poisoning. However, the reviewer would like to offer the thought that, while one of the most widely cited barriers is the cost of Pd metal, this is in effect an upfront cost. The Pd will ultimately be easily recoverable and, if the metal price has risen during the lifetime of the membrane, could be considered to be an investment.

Reference

1 Johnson Matthey Gas Purification Technology: http://www.jmgpt.com/html/all_data_sheets_link.html

The Reviewer

Dr Hugh Hamilton has worked at the Johnson Matthey Technology Centre for nearly 19 years, during which time he has researched in a range of areas including autocatalysts, palladium membranes, fuel cell MEA manufacture and hydrogen storage. His current role includes sorbent development for Hg from syngas and Ti powder metal injection moulding process development.