INORGANIC MEMBRANES SYNTHESIS, CHARACTERISTICS AND APPLICATIONS

By

Ramesh R. Bhave, Ph.D

VNR VAN NOSTRAND REINHOLD

New York

Library of Congress Catalog Card Number 91-18774
ISBN 0-442-31876-6

Manufactured in the United States of America

Published by Van Nostrand Reinhold
115 Fifth Avenue
New York, New York 10003

Chapman and Hall
2-6 Boundary Row
London, SE1 8HN, England

Thomas Nelson Australia
102 Dodds Street
South Melbourne 3205
Victoria, Australia

Nelson Canada
1120 Birchmount Road
Scarborough, Ontario M1K 5G4, Canada

16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

Library of Congress Cataloging-in-Publication Data

Inorganic membranes: synthesis, characteristics, and applications/
edited by Ramesh R. Bhave.
p. cm.
Includes bibliographical references and index.
ISBN 0-442-31876-6
1. Membranes (Technology) I. Bhave, Ramesh R., 1952-.
TP159.M4I56 1991 91-18774
660'.2842--dc20 CIP

Contributors*

Prof. Anthony J. Burggraaf, Ph.D, The University of Twente, Laboratory for Inorganic Chemistry, Material Science and Catalysis, Enschede, The Netherlands

Prof. B. Tarodo de la Fuente, Ph.D, University of Montpellier, Sciences et Techniques du Languedoc, Montpellier, France

Jacques Gillot, Societe des Ceramiques Techniques, (a subsidiary of Alcoa Separations Technology, Inc.) Tarbes, France

Jacques Guibaud, Societe des Ceramiques Techniques, (a subsidiary of Alcoa Separations Technology, Inc.) Tarbes, France

H. Phillip Hsieh, Ph.D, Alcoa Laboratories, Alcoa Center, Pennsylvania

Klaas Keizer, Ph.D, The University of Twente, Laboratory for Inorganic Chemistry Material Science and Catalysis, Enschede, The Netherlands

Prof. Michel Rumeau, University of Montpellier, Laboratoire Genie des Procedes Montpellier, France.

Robert J. Uhlhorn, Ph.D, The University of Twente, Laboratory for Inorganic Chemistry, Material Science and Catalysis, Enschede, The Netherlands (currently with UNILEVER, Detergents Division, Netherlands)

Venkat K. Venkataraman, Ph.D, U.S. Department of Energy, Morgantown Energy Technology Center, Morgantown, West Virginia, (*formerly* with Norton Company and Millipore)

Vassilis T. Zaspalis, Ph.D, The University of Twente, Laboratory for Inorganic Chemistry, Material Science and Catalysis, Enschede, The Netherlands

* (please note that contributors affiliation does not indicate that the **work is** supported by the contributors organization)

Foreword

Conventional separation techniques such as distillation, crystallization, filtration or solvent extraction were enriched in the 1960s by another class of processes which uses membranes as the principal separation elements.

The term membrane covers a great variety of materials, structures and geometries; the membrane acts as a selective barrier; under the effect of a driving force, on contact with chemical mixtures, it allows the separation of the constituents as a function of their specific transfer properties and is thus described as permselective.

Membrane separation techniques are very attractive and, in many cases, faster, more efficient and more economical than conventional processes, as the fractionation takes place without a phase change. Their use is expanding rapidly and the average annual growth rate over the next decade is estimated to be 10%.

Inorganic membranes for separations in liquid media appeared on the market in the beginning of the 1980s. These were porous, permeable, ceramic-type membranes with a composite structure and were called 3rd generation membranes to distinguish them from the purely organic membranes, which were the only ones used until then in separation applications.

The launching of this new generation of membranes was relatively slow; in the symposia and conferences on membrane separation techniques they occupied a relatively marginal place. It was only in 1989 that the First International Conference on Inorganic Membranes (ICIM) was organized at Montpellier (France). However, no basic text on the science and technology of inorganic membranes has yet been published.

This book by Dr. Ramesh R. Bhave will very well fill this gap. In the different chapters contributions by specialists, who are recognized authorities in the international research or industrial community, are included to treat all aspects relating to inorganic membranes very completely and objectively: from their history to fundamental phenomena, from methods of synthesis to characterization techniques and from present applications to medium- and long-term perspectives in separation processes or chemical reactions.

Research workers and engineers will find precise answers to their requirements and will also be able to thoroughly study specific points by using the extensive list of references at the end of each chapter.

Historically, it was in 1958, in the Second International Conference on the Peaceful Uses of Atomic Energy at Geneva, that the first papers on the production and the characterization of inorganic membranes were presented and discussed.

The French Atomic Energy Commission was particularly interested in the production of different kinds of microporous materials, metallic or ceramic, obtained by various techniques, from powder technology to the anodic oxidation of aluminum or chemical treatment of alloys. It recommended, in addition, the concept of a composite membrane, which was the only means of combining high permeability with mechanical strength.

This work was undertaken as part of the program for the separation of uranium isotopes by gaseous diffusion of uranium hexafluoride vapor. Paradoxically, it showed that the requirements for the porous texture of membranes used in ultrafiltration and microfiltration for separation in liquid media were similar to those of the components of gaseous diffusion barriers.

With the cooperation of industrial ceramic firms, the first uranium enrichment plant was put into operation in 1966 and the European Eurodif plant was operational in 1978. This plant, with more than 120 million barriers, the equivalent of 4 million square meters of installed surface, is believed to be the largest in the world equipped with inorganic membranes.

It is not, therefore, entirely fortuitous that the principal industrial firms that produce different types of inorganic membranes for ultrafiltration and microfiltration were involved in the French uranium enrichment program.

The development of ultrafiltration and microfiltration separation techniques using inorganic membranes had a laborious beginning. Gaining a foothold in a market dominated by organic membranes was difficult. It was necessary to convince industry that the additional cost of the inorganic membranes was largely compensated by greater lifetime or higher reliability.

In many situations the inherent properties of inorganic membranes clearly made them the only potential solution. It was here that inorganic membranes took birth in diverse applications involving agro-food, biotechnology and pharmaceutical products. It is believed that the development of membranes with higher selectivities, the nanofiltration membranes, will contribute to extend their use in the above listed relatively established fields and to a greater use in the chemical and petroleum industries and in environmental applications.

It was also possible, through the modifications of membrane surface, (which altered the wetting characteristics and surface charge), to produce an organic–inorganic membrane. These membranes may offer excellent mechanical and thermal resistance with the additional advantage of greater flexibility due to functionalization of organic radicals.

One of the essential improvements is the control of the interactions between the solution deposited on the pore walls to limit plugging and thus to increase the flux through the membrane. Another unique feature of charged organic–inorganic ultrafiltration membranes is their ability to combine one or more separation mechanisms. These membranes may also find use in environmental applications.

A major advantage of inorganic membranes lies in the possible applications of the numerous methods for studying porous membranes and separation barriers which have been perfected in France and the United States. These methods, in particular, have enabled the characterization of their intrinsic properties accurately and reproducibly.

This characterization, used profitably in determining the important production parameters, can ensure excellent control of the fabrication process and also allow the quantitative determination of possible anomalies under plant operating conditions. The ability to characterize inorganic membranes have enabled membranologists to obtain solutions to many problems by a less empirical approach.

Inorganic membranes also show significant potential for use in fields other than separation in liquid media. In the fractionation of gases or vapors, outside of isotopic separation, inorganic membranes allow us to envisage applications thanks to the advances in materials science and knowledge of surface phenomena and transport phenomena. In some situations, the selectivity is greatly influenced by the differences in surface fluxes or the preferential capillary condensation of the species being separated.

Recently, another method for the separation of gases, frequently described as "facilitated" transport membranes, using molten salts immobilized in inorganic (e.g. ceramic) porous supports has been studied.

A particularly innovative application of inorganic membranes is their use as a conversion catalyst in chemical syntheses, with or without separation of the species formed.

Inorganic membranes have established their use in a number of commercial applications involving agro-food, biotechnology and pharmaceutical products. However, the present development efforts to produce high-selectivity nanofiltration membranes, the perspectives for new chemical and environmental industry applications and the potentialities in the separation of gases or in chemical syntheses will hasten the deployment of inorganic membranes in separations. The annual growth rate for the use of inorganic membranes alone, is estimated to be in the range 15–20% over the next decade.

To fully realize its potentialities, the science of inorganic membranes will require contributions from many different fields: materials science, hydrodynamics, physical chemistry of surfaces and chemical engineering, thus necessitating the cooperation of groups of specialists.

There is no doubt that this first comprehensive volume describing the synthesis, characterization and applications will make their advantages and possibilities better known, will contribute to their development and will give rise to new collaborations. It will also be very useful to future users of inorganic membranes and will allow them to include membrane techniques in the research and optimization of their processes, with the assurance of respect for the environment.

Jean Charpin, Ph.D
CEA, France

Prof. Louis Cot
University of Montpellier,
France

Preface

Inorganic membranes, since their introduction to commercial applications in the early 1970s, are making rapid inroads in many areas such as food and beverage processing, biotechnology applications and water treatment. There are also a couple of emerging areas such as the use of inorganic membranes in high-temperature gas separations and catalytic reactors.

As the use of inorganic membranes has expanded, a large number of publications covering a variety of subjects have appeared in the literature. This project was undertaken to fulfill the need to organize and present the wealth of information in a single reference volume describing the state-of-the-art in the development of inorganic membrane technology.

The book can be used by any scientifically trained individual interested in the field of inorganic membranes. The simple treatment of all subject matter will help the inexperienced user to easily comprehend the technical information presented in the book. The book will also serve as a useful reference volume for chemical engineers, chemists and technicians as well as business managers familiar with membrane separations.

I have been fortunate to be associated in the field of membrane separations for the past ten years. The past five years of my research and development efforts have been devoted to the emerging field of inorganic membranes. I have been truly intrigued by the great potential these materials show to solving difficult processing problems, including hostile environments where materials of high mechanical strength and structural integrity are required. Although inorganic membranes today enjoy only a small fraction (~ 5%) of the total membrane market, by the year 2000 their market share is expected to increase to about 10–12%.

In late 1987 when VNR first approached me to write the book, what inspired me most was the opportunity to describe and critique the developments in this continuously evolving field that holds great promise to displace conventional technologies with significant economical and technological advantage.

This book represents the first effort to document the available information in a logical and systematic fashion with in-depth technical discussion of fundamental principles and technical aspects related to the use of inorganic membranes. The subject matter is vividly illustrated through the use of numerous documented research and development studies describing specific membranes, material properties or applications. I hope that the book will serve to fulfill the needs of both current and prospective users in aspects related to the synthesis, characteristics (including characterization techniques) and applications.

The first chapter of the book is meant to provide the reader with a historical perspective on the developments in the field of inorganic membranes, which date back to the 1940s. The first application of inorganic membranes (and incidentally the world's largest) was for the enrichment of ^{235}U from an isotopic mixture of $^{235}UF_6$ and $^{238}UF_6$ by gaseous diffusion. The first commercial use of inorganic membranes was not realized until the early to mid-1970s for liquid separations using microfiltration or ultrafiltration membranes.

A large number of membrane synthesis techniques have been explored, developed and commercialized in the past 15–20 years. Chapter 2, on the synthesis of inorganic membranes, covers many aspects of these product research and development efforts in detail. The reader is provided with an overview of basic principles, theoretical aspects and membrane modification techniques. This may be helpful in the proper selection of membranes to suit specific application needs.

The general characteristics of inorganic membranes are reviewed in Chapter 3. Microstructural aspects such as pore diameter, thickness and membrane morphology are described along with consideration of material characteristics particularly those related to chemical, surface and mechanical properties.

The next two chapters (Chapters 4 and 5) are devoted to a thorough discussion of liquid permeation and separation, operating considerations and the design of filtration systems. During membrane filtration a variety of phenomena influence flux and/or separation behavior. These are identified and treated in some detail. A good understanding of fouling mechanisms can be very helpful in minimizing flux decline and in the proper selection of pore diameter and operating conditions.

Models for the prediction of microfiltration and ultrafiltration flux are described. Parameters influencing solute retention properties during ultrafiltration are identified and the subject is treated in some detail with illustrative examples.

In Chapter 5, cross-flow membrane filtration is described in detail to help the user understand the influence of important operating parameters on system performance. A few commonly used operating configurations are also described to point out their specific advantages or limitations. In addition, some aspects of system design and operation are discussed which can substantially influence system performance.

The current development status in the two emerging areas of gas separations and catalytic membrane reactors is reviewed in Chapters 6 and 7, respectively. Although inorganic gas separation membranes have been employed in nuclear (defense-related) applications, their use in commercial applications is yet to be realized. This is largely due to the lack of suitable commercial membranes with acceptable flux and/or separation performance under industrial conditions. The fundamentals of gas separations under various separation mechanisms are reviewed.

Another emerging area that is gaining considerable attention is the use of inorganic membrane reactors to enhance the productivity of chemical processes which are otherwise limited by thermodynamic constraints. The technical feasibility of high-temperature catalytic membrane reactors is being evaluated at the laboratory scale for a number of industrially important processes. Substantial development efforts are required to realize the full potential of inorganic membranes in commercial gas phase separations. The subject of liquid phase catalytic membrane reactors is not covered here due to the relatively few publications describing the use of inorganic membranes in these situations.

Key technical barriers are the production of small pore diameter (1–2 nm or smaller) porous composite membranes or high-flux dense membranes, and long-term high-temperature stability under industrial operating conditions. In addition, the design and fabrication of membrane elements, housings and seals will also pose significant technical challenges. Despite these difficulties, R & D efforts continue worldwide to develop improved membrane structures, since only inorganic membranes offer the possibility to withstand high-temperature processing environments. It is anticipated that a few of these applications will become commercially viable by the turn of the century.

Yet another emerging application is the use of composite ceramic membranes as gas filters (e.g. Membralox® alumina membranes) in the microelectronics industry. In this application, industrial gases are required to be purified to exceptionally high-purity levels. There are no published reports describing the performance of ceramic gas filters at this time. For this reason, applications of ceramic gas filters are not described in the volume. As this potentially rewarding area grows in the next few years their performance descriptions will most certainly appear in the scientific and technical literature.

The last two chapters of the book (Chapters 8 and 9) describe commercial and developing liquid phase applications (primarily filtration) that span many diversified industries. At the present time, almost all industrial plants using inorganic membranes are concerned with liquid phase separations. A large majority of these industrial filtration plants are in food, dairy and beverage processing. Biotechnology-related applications are still largely under development with a few exceptions such as cell harvesting and enzyme separations. Chapter 8 provides a complete review of all important commercial and developing food and biotechnology applications. Inorganic membrane performances in many other applications are not described in the open literature due to proprietory considerations.

The use of inorganic membranes for the filtration of water, wastewater treatment and chemical process industry filtration applications is covered in Chapter 9. The filtration of surface and groundwater to produce potable water is perhaps the most prominent industrial application. The treatment and/or recovery of oils from oily wastes and oil–water microemulsions is an area which has received a great deal of attention with some commercial success.

In the 1980s, a substantial number of inorganic membrane manufacturers emerged. A complete list of inorganic membrane manufacturers and their locations is given in the Appendix.

The contributions made in this volume by the author represent his personal and professional views and technical interpretations largely based on published work. These do not in any way reflect the views or endorsements by Alcoa Separations Technology, the author's current employer. This is also true of all contributors to this volume.

I want to express deep appreciation to Terry Dillman of Alcoa Separations for his personal interest and support. I also want to take this opportunity to thank A. J. Burggraaf, J. Gillot, J. Guibaud, H. P. Hsieh, K. Keizer, R. Rumeau, B. Tarodo de la Fuente, V. Venkataraman, R. Uhlhorn and V. Zaspalis for their extremely valuable contributions to this volume. Needless to say that without their cooperation and support it would not have been possible to present a comprehensive treatment of the developments in this emerging field, from membrane synthesis to gas and liquid phase applications.

I want to especially acknowledge the strong support and many sacrifices of my wife, Seema, during the writing of this book. Her understanding and appreciation made it possible to complete this project which consumed many many weekends, evenings and nights.

I also want to express my sincere appreciation to the VNR editorial staff and particularly to Marjorie Spencer and Alberta Gordon, for their patience, advice, and encouragement throughout the course of publication of this volume.

Contents