

Inorganic membranes for hydrogen isotope-helium separation in fusion energy research

Rupsha Bhattacharyya

Heavy Water Division, Bhabha Atomic Research Centre, Mumbai-400085, (INDIA)

E-mail : rupshabhattacharyya1986@gmail.com

ABSTRACT

Inorganic membrane based techniques have been applied to various gas separation processes in the chemical process industries, especially in the separation of hydrogen from hydrocarbons and carbon dioxide in synthesis gas. In the field of fusion energy research, the separation of hydrogen isotopes, especially deuterium and tritium from a helium stream is of great importance since helium is the inert carrier gas that will purge the tritium bred during fusion from the lithium-containing solid and liquid breeder materials. The efficiency of separation of tritium from helium is a major factor that governs the success of fusion energy systems. Membrane based processes have been studied quite extensively for this separation because of the very high selectivity for hydrogen isotopes that is obtained in this technique as compared to more conventional methods. This review summarises current information about the types of membranes studied for hydrogen separation, their synthesis and characterization methods, the desirable properties of these membranes and the technological difficulties associated with this separation method. Specifically, the suitability of different types of membranes for tritium removal from helium is ascertained in this work. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Gas separation;
Membrane;
Tritium;
Palladium membrane;
Ceramic membrane.

INTRODUCTION

Separation of components of a gaseous mixture is often a vital step in the chemical process industries. Some well-known examples include separating nitrogen and oxygen from air, recovering helium from natural gas, and separating hydrogen from its mixture with hydrocarbons or carbon dioxide or ammonia. While conventional separation techniques like distillation and adsorption are being widely used in gas processing industries, there are some relatively new techniques like membrane based separation processes which are fast becoming competitive with the more conventional methods^[1,2]. In

the petroleum and petrochemical industries hydrogen separation from other gases by membrane technology is routinely practised. Thus various types of membranes (e.g. polymeric, metallic, ceramic etc.) for hydrogen separation have been developed and studied^[3-8]. With enhanced emphasis on hydrogen as a major energy carrier in the near future, hydrogen generation techniques and its separation from various other gases will only gather increasing attention. In the field of fusion energy research (as in the ITER project), the separation of tritium (which is an isotope of hydrogen that is a fuel for fusion and is also generated during fusion by interaction of high energy neutrons with lithium contain-

ing breeder materials) from helium is envisaged to be a very important step is making a fusion reactor system self sufficient in its tritium requirements^[9-12]. Tritium that is bred in solid and liquid breeder materials has to be recovered from the helium stream and recycled back to the plasma chamber for another cycle of plasma operation and fusion reactions. There are several options for this separation like chromatographic processes, distillation, thermal diffusion technique and membrane based separations. TABLE 1 presents a general comparison of these processes^[1,2]. It is seen that the selectivity and

ease of operation of the membrane based process are the highest and since for fusion energy applications this are factors of great importance, so feasibility of membrane separation operations have been quite extensively studied for this application. In this paper a brief review of information pertaining to membrane based hydrogen separation is presented. Membrane preparation techniques, characterisation of membrane properties and the difficulties or challenges in using them for separation of helium and hydrogen isotopes in fusion energy sector have been discussed.

TABLE 1 : Comparison of methods of separating hydrogen and its isotopes from helium gas^[1,2]

Process	Advantages	Disadvantages
Gas chromatography and cryogenic distillation	Both are well established technologies, helium itself can act as the carrier gas and no other gas is needed, relatively inexpensive materials like molecular sieves can be used as the stationary phase in chromatography	Low temperature (around 25 K for distillation and 100 K for chromatography) needed, so process is energy intensive and expensive, with special insulation and instruments needed
Thermal Diffusion	No other materials as separation agents need to be used except for a chamber with the necessary thermal gradient created inside it	Effectiveness of separation depends on the temperature difference created, collection of separated gases is complicated and can lead to mixing again
Reversible metal hydride based getter beds	High selectivity for hydrogen and its isotopes as helium will not be adsorbed, forms a separation system as well as a low pressure system for long or short term storage of the hydrogen isotope	Involves handling of pyrophoric, toxic materials, specially designed complex vessels with efficient heating and cooling arrangements needed for hydrogen uptake and on-demand release, thus high requirement of heat energy during recovery
Pressure swing adsorption technology	With the use of selective adsorbents, the separation can be quite efficient, relatively lower operating pressure required, high hydrogen content in feed can be economically handled	Systems are large, complex operating philosophy, several adsorber beds have to be present in the system to ensure continuous operation, low recovery of hydrogen isotopes
Noble metal based membrane systems	Extremely high selectivity and high recovery for hydrogen isotopes are possible, hence high purity (> 99.99 % by volume) of hydrogen obtained, handles high fluxes of hydrogen, modular design of separation units possible, high ease of operation, no phase change operation takes place	High temperatures are needed for better separation, expensive noble metals required, material development and optimization still on-going, possibility of membrane fouling by contaminants in feed gas, very high pressure required on the feed side and low pressure needed on the permeate side, recovered product from the permeate side may have to be recompressed before further applications, lower capital and maintenance costs may be offset by higher energy requirement of compression

TYPES OF MEMBRANES FOR HYDROGEN ISOTOPE SEPARATION

A wide variety of inorganic membranes for gas separations, especially separation of hydrogen from gases like carbon monoxide, hydrocarbons and inert gases like nitrogen, helium etc have been developed

and studied^[13]. Hydrogen and helium are quite close in terms of molecular weight and atomic size, so in their separation the size sieving effect is expected to have less of a role. The solution-diffusion effect in a material that is highly selective for hydrogen and its isotopes is possibly the only effect that can be effectively utilised in a membrane based separator for hydrogen and helium. For this reason, metallic membranes have been studied

Review

most extensively for applications in the field of fusion research. The major types of membranes and their features and synthesis techniques are briefly reviewed in the following sections.

Metallic membranes

Membranes made of palladium and alloys of palladium with metals like silver, copper and some rare earth elements have been studied widely as separating agents for hydrogen from its mixtures with other gases like helium, nitrogen, hydrocarbons and others. The most significant advantage that these membranes offer is the very high selectivity for hydrogen and its isotopes, though the very high cost of these materials is the major deterrent in their use. The metallic membranes are generally used in the form of sheets or films supported on ceramics or similar porous substrates and thus they are generally referred to as composite membranes which offer mechanical strength, rigidity and highly selective hydrogen transport characteristics^[12]. The metallic film presents certain active sites which catalyse the dissociation of hydrogen molecule into atoms. It is in this atomic form the hydrogen is ultimately transported across the thickness of the membrane and ultimately recombined on the other side^[12]. This is what gives rise to the high selectivity of metallic membranes for hydrogen, thus making this one of the best ways to separate hydrogen isotopes from helium for fusion applications. Palladium alone has nearly 100% selectivity for hydrogen but it is also highly susceptible to hydrogen embrittlement. This reduces the useful working life of the membrane system. Embrittlement is partially tackled by the use of alloying elements like silver, copper or gold to the extent of 20 to 25% by weight in palladium which provide some degree of mechanical strength^[14]. Other than these elements, rubidium, yttrium, indium, ruthenium have also been alloyed with palladium for use as hydrogen separating membranes^[14-16]. The selectivity and hydrogen permeation rate both depend on the alloy composition and for each type of alloy, an optimal ratio of palladium to alloying element can be determined^[17].

Supported metallic membranes are synthesised by a variety of techniques like electroless plating, sputtering, physical and chemical vapour deposition and thermal evaporation^[13,18]. Surfactant induced electroless plating techniques have also been studied recently^[19].

Multilayer membranes consisting of palladium layers on either side of a Group V metal like zirconium, niobium or tantalum have been also been studied^[20]. Such membranes combine the benefits of higher rates of hydrogen diffusion through the intermediate metal layer with the high selectivity of the palladium on the top surfaces.

The usual support materials studied include both metallic supports like porous nickel or porous sintered steel^[13,21-23] as well as ceramic oxides like alumina, yttria stabilized zirconia (YSZ) and silica^[13,24-28]. The support has been found to have significant effect on the permeation rate of hydrogen through the membrane. A highly porous structure facilitates hydrogen transport while the ability of the support to sustain high operating temperatures and pressures without mechanical damage allow efficient use of the composite membrane system for separation applications.

Palladium based membranes are the most widely studied membrane systems for hydrogen isotope (deuterium and tritium)-helium separation in fusion research. Experimental work, theoretical modelling and simulation leading to conceptual and actual design of membrane based separation units for tritium and helium have been performed^[50-57]. The typical operating temperatures reported for hydrogen separation using palladium based membranes range from 500 to 900 K while pressures are around 500 hPa to 100 kPa^[52,58]. Membrane thicknesses are typically from few microns to over 100 micron^[58].

Membrane separations are carried out in modular units and various module configurations are available. These include flat sheets, hollow fibres and spiral wound units. The use of a particular module for hydrogen separation from helium would depend on the required throughput, desired flow pattern, required selectivity for hydrogen and the operating conditions (temperature, feed and permeate side pressure). Various designs of the gas separation membrane modules and their relative advantages and disadvantages have been well documented in literature^[61,62].

Ceramic membranes

Ceramic membranes represent another major class of materials that have been studied in the context of hydrogen separation at intermediate and high temperatures. In literature these membranes are commonly re-

ferred to as dense ceramic membranes with mixed proton and electron conductivity^[29-33]. Put very simply, these materials are mainly complex oxides^[34] and other than membrane based separation for hydrogen, such materials have been extensively investigated in the context of solid oxide fuel cells as they constitute the solid electrolyte in these cells^[35]. Discussion here pertains to only the non-electrical and highly selective transport of hydrogen across the membranes using a hydrogen partial pressure gradient across the membrane as driving force, thus enabling its recovery from gas mixtures. These materials are somewhat cheaper than metallic membranes made of palladium and its alloys, though they may be more difficult to fabricate since it involves several steps. Moreover they lack mechanical strength by themselves so they too require porous supports or they have to be dispersed within a rigid porous matrix that provides the support.

Chemically most of the ceramic membranes consist mainly of SrCeO_3 , BaCeO_3 , SrZrO_3 , BaZrO_3 perovskites^[30] and have various doping elements like cobalt and nickel incorporated into them^[30,31]. These membranes are thus composites of ceramics and metals and are thus often referred to as cermets. The ceramic component of the membrane is proton conducting and the metallic dopants like nickel enhances electrical conductivity of the cermet and also provides it with mechanical stability and allows for dissociation of molecular hydrogen and its recombination on the other side of the membrane matrix^[32,42]. Even without the presence of metallic species as dopants, the ceramic structure must provide suitable active sites for the dissociation and association of hydrogen into atoms, though in most cases that does not suffice and suitable surface modification through coatings or doping is essential^[38]. For the purpose of characterising the electrical properties of exclusively the ceramic part, sometimes only pastes or thin films are coated onto the surfaces of the membranes without actually incorporating metal ions in the bulk of the ceramic^[33]. Apart from zirconates and cerates, various other types of cermets like indium doped niobium phosphates^[41] and $\text{Nd}_5\text{LnWO}_{12}$ and have also been investigated as potential materials for hydrogen separation membranes^[43]. The fabrication techniques for these membranes are explicitly described in existing literature^[29-43].

As has already been mentioned above, the transport of hydrogen through ceramic membranes is carried out without depending on an external electrical circuit, so the rate of hydrogen permeation depends greatly on the membrane's protonic and electronic conductivities. The conductivity arises intrinsically from the presence of defects in the material. The proton conductivity is generally the limiting factor^[31] but materials having high proton conductivity generally suffer from low electronic conductivity^[38]. Acceptor doped cerate membranes have high proton conductivity but low chemical stability. Inclusion of zirconates in the membranes improves the chemical resistance of the material^[31]. The detailed mechanisms of proton and electronic conductivity of these materials have been well explained by several researchers^[36-38]. Various ways of enhancing the electronic conductivity of perovskite based ceramic proton conductors have been mentioned in literature^[38].

Most of the work on proton conducting membranes for hydrogen separation pertains to fields like reforming of natural gas, coal gasification and so on i.e. the hydrocarbon industry. There have been relatively fewer studies involving ceramic membranes, carried out for examining the feasibility of hydrogen isotope-helium separation in fusion energy^[44-46], though Perovskite type ceramics have been studied for development of hydrogen sensors and electrochemical pumps^[47-50]. The membranes exhibit highest conductivities at about 900 to 1000 °C temperature but these are very high temperatures not likely to be encountered in the tritium management systems of fusion plants. With the development of ceramics with good conducting behaviour at intermediate temperature ranges (e.g. 300 to 600 °C), the interest in these materials is expected to grow since the typical temperature of the tritium-helium gas stream in the ITER plant is expected to be around 350 to 450 °C^[59,60].

For proton conducting ceramic membranes, a problem that is encountered is the conduction of the oxygen ion that increases with increasing temperature of operation^[36,37]. This has led to the study of oxygen deficient perovskite structures for membrane applications. For fusion applications, deuterium-tritium has to be removed from helium and this gas mixture is not likely to contain any significant additional source of moisture or gaseous oxides. Thus control of the oxygen ions in the

Review

membrane material should largely alleviate the problems of oxygen ion conduction that so drastically affects proton and electron conduction.

Carbon based membranes

Carbon based membranes fall in the category of porous membranes as opposed to the metal and ceramic membranes which have dense structures^[63]. These membranes have an advantage over metallic membranes in that they are significantly less expensive and also the flux of hydrogen through them is directly proportional to the pressure as compared to a square root dependence on pressure for metal membranes. They are also capable of operating at higher temperature and pressure ranges than the other membranes for hydrogen separation and are chemically more resistant^[64,70]. One problem with them is the strong adsorption of organic vapours on these membranes and that has a poisoning effect on membrane behaviour^[63]. This necessitates frequent degassing operations prior to membrane use but this may not be a problem in case of fusion research since organic vapours are much less likely to be present as contaminants in the gas stream. Also the higher permeation rates come at the cost of lower selectivity and consequently less pure gas streams on the permeate side. Moreover these materials are very brittle and can crack during the pyrolysis step itself. Carbon membranes have been studied in the form of supported and unsupported membranes, nanotubes, fibres and carbon molecular sieves^[12]. Thus both surface diffusion and molecular size based sieving govern the transport of gases across them^[64].

The most general preparation technique for carbon membranes involves high temperature pyrolysis of a carbon precursor like a polymer, coal, resin or graphite in inert atmosphere or under vacuum^[12,63]. The porous structure arises from the escaping gas molecules formed during the pyrolysis process^[69]. Chemical vapour deposition of carbon on a porous support has also been used as a synthesis technique^[71]. More recently, grapheme oxide based ultra thin membranes have been reported for hydrogen separation^[68]. The choice of starting materials governs the ultimate properties of the membrane produced. Nanoporous carbon membranes using selective surface flow have been studied in the context of separating hydrogen from hydrocarbons^[65,66] but it is

not very likely to be useful for separating hydrogen from helium, especially at the low feed concentrations to be handled in fusion energy programs because the difference in molecular weights between the species is not significant. Activated diffusion is the mechanism of transport reported for these membranes. Carbon nanotube based membranes allow higher gas transport rates because of their inherently smooth interiors. The selectivity can be improved by functionalizing the tips or ends of the tubes through appropriate chemical treatment^[67]. Carbon molecular sieves have also been used as membranes for gas separations. Various preparation techniques and values of permeability and selectivity achieved with these membranes have been described in literature^[72-75]. Carbon based membranes are definitely advantageous as compared to polymeric membranes for hydrogen separation and they can also be synthesised from a wide variety of starting materials which gives one the option of investigating low cost organic precursors for membrane synthesis.

The advantage of higher permeation fluxes in carbon based membranes is obtained at high temperatures at which metal membranes may sinter. But it is unlikely that such high temperatures will be encountered in the fusion energy research, thus rendering the advantage of carbon membranes unusable. This is possibly the major reason why such membranes have not been given much attention in this context.

CHALLENGES IN MEMBRANE BASED SEPARATION OF HYDROGEN ISOTOPES AND HELIUM

Membrane based separation of hydrogen from gas mixtures is a well known and widely used process in the hydrocarbon industry. Its future is promising in the fusion energy sector as well. With the possibility and the need to have a hydrogen based economy in the not so distant future, there is an urgent need to study such separation systems with even greater interest. But there are several technical challenges to be overcome before membrane based separations become economically more viable.

i) The first and the most obvious issue lies with the cost of the materials used for preparation of membranes and the complexity of the preparation meth-

ods. Be it metals, ceramics, carbon or zeolite based membranes, none of the options are low cost when high selectivity, high purity and high permeation rates required for large scale applications have to be achieved. Moreover a number of dry and wet steps are also generally involved in the synthesis and they are not always easily scaled up from laboratory level to industrial level operations. Fabrication of the membrane modules is also quite difficult since the membrane itself has to be handled with great care and under stringently controlled conditions which may be quite difficult to achieve at the commercial plant level. Achieving reproducible membrane properties like morphology, structure and pore size distribution in every batch is also not a simple task, thus properties like selectivity and permeation rate may vary greatly and affect the overall separation process.

- ii) The propensity of membranes to poisoning by gases like water vapour, carbon monoxide, hydrogen sulphide, and sulphur dioxide is yet another problem. Poisoning adversely and dramatically affects selectivity for hydrogen and thus renders the separation ineffective. This is especially the case with metallic membranes. In the fusion energy field there is less possibility of such contaminants being present in the helium gas stream though moisture could be present if it is released from the solid breeders or if it somehow makes its way into the helium stream from water based coolers. Thus poison resistant membranes are highly desirable.
- iii) Membranes for gas separation should be thin to allow a higher gas permeation rate. But this makes them mechanically weak and prone to damage, crack formation and tears. That allows hydrodynamic gas flow i.e. bulk flow of gas and no separation is possible. Thicker membranes would be more expensive and lower the permeation flux. Thus membranes supported on porous structures are used though this makes the system more bulky. Also the membrane and support should be chemically and mechanically compatible under the expected operating conditions.
- iv) The embrittlement of metals in hydrogen service is a very common problem. Hydrogen is also quite strongly adsorbed by many metals including palla-

dium and this leads to phase change of the metal upon adsorption of a certain volume of hydrogen. This adversely affects membrane properties and leads to their damage and loss of separation capability. In fusion energy research, the concentration of hydrogen isotopes in the helium stream is not expected to be very high (about a few percent), so the problems of membrane embrittlement will be expected to be less severe over the expected operating life of a fusion plant like ITER.

- v) In fusion energy research the separation of deuterium and tritium have to be accomplished from helium. Most experimental work involving membrane separations has been confined to the use of hydrogen. With the heavier isotopes of hydrogen the ratio of transport rates of the species and hence the selectivity will be brought down, thus making the actual separation more difficult. Moreover there is a possibility of radiation damage to the membranes from the beta particle emission from tritium. All these are causes for uncertainty in the design of the hydrogen isotope-helium separation system.

SUMMARY AND CONCLUSIONS

Membrane based separation is a promising technique for separating hydrogen isotopes from helium. Presently noble metals and their alloys are most widely used to accomplish this but less expensive options like ceramic and carbon based membranes have also been extensively studied. Several membrane synthesis techniques have been developed and various kinds of membrane modules have been put into practice. There are technological challenges to be overcome before the separation system becomes more cost effective and these are expected to provide the impetus necessary for researchers to continue to explore this ever-diversifying field.

ACKNOWLEDGEMENTS

The author wishes to thank Dr Sadhana Mohan, Mr. Kalyan Bhanja and Mr. Sandeep K.C. of the Heavy Water Division, BARC for introduction to the field of membrane based separation of hydrogen from helium and for providing inspiration to write the current review.

REFERENCES

- [1] R.R.Zolanz, G.K.Fleming; Gas Permeation, in W.S.Winston Ho, K.K.Sirkar, (Eds); Membrane Handbook, Van Nostrand Reinhold, New York (NY), 19-100 (1992).
- [2] K.Scott; Handbook of Industrial Membranes, 1st Editon, Elsevier Science Publishers Limited, London (UK), (1995).
- [3] G.Q.Lu, J.C.Diniz da Costa, M.Duke, S.Giessler, R.Socolow, R.H.Williams, T.Kreutz; J.Colloid Interface Sci., **314**, 589 (2007).
- [4] S.A.Stern; The Separation of Gases by Selective Permeation, in Patric Meares, (Ed); Membrane Separation Processes, Elsevier Scientific Publishing Company, Amsterdam (The Netherlands), 295-326 (1976).
- [5] K.Keizer, R.J.R.Uhlhorn, T.J.Burggraaf; Gas separation using Inorganic Membranes, in R.D.Noble, S.A.Stern, (Eds); Membrane Separations Technology. Principles and Applications, Elsevier Science B.V., Amsterdam (The Netherlands), 553-586 (1995).
- [6] R.Spillman; Economics of Gas Separation Membrane Processes, in R.D.Noble, S.A.Stern, (Eds); Membrane Separations Technology. Principles and Applications, Elsevier Science B.V., Amsterdam (The Netherlands), 589-668 (1995).
- [7] S.P.Nunes, K.V.Peinemann; Gas Separation with Membranes, in S.P.Nunes, K.V.Peinemann, (Eds); Membrane Technology in the Chemical Industry, WILEY-VCH Verlag GmbH, Weinheim (Federal Republic of Germany), 39-67 (2001).
- [8] D.J.Stookey; Gas Separation Membrane Applications, in S.P.Nunes, K.V.Peinemann, (Eds); Membrane Technology in the Chemical Industry, WILEY-VCH Verlag GmbH, Weinheim (Federal Republic of Germany), 95-126 (2001).
- [9] M.A.Fütterer, H.Albrecht, P.Giroux, M.Glugla, H.Kawamura, O.K.Kveton, D.K.Murdoch, D.Sze; Fusion Engg.Des., **49-50**, 735 (2000).
- [10] M.Glugla, L.Dörr, R.Lässer, D.Murdoch, H.Yoshida; Fusion Engg.Des., **61-62**, 569 (2002).
- [11] M.Glugla, A.Antipenkov, S.Beloglazov, C.Caldwell-Nichols, I.R.Cristescu, I.Cristescu, C.Day, L.Doerr, J.P.Girard, E.Tada; Fusion Engg.Des., **82**, 472 (2007).
- [12] M.W.Ockwig, T.M.Nenoff; Chem.Rev., **107**, 4078 (2007).
- [13] S.Yun, S.T.Oyama; J.Membr.Sci., **375**, 28 (2011).
- [14] D.Fort, J.P.G.Farr, I.R.Harris; J.Less-Common Met., **39**, 293 (1975).
- [15] G.S.Burkhanov, N.B.Gorina, N.B.Kolchugina, N.R.Roshan, D.I.Slovetsky, E.M.Chostov; Platinum Metals Rev., **55**, 3 (2011).
- [16] S.Ryi, A.Li, C.J.Lim, J.R.Grace; Int.J.Hydrogen Energy, **36**, 9335 (2011).
- [17] F.Roa, M.J.Block, J.D.Way; Desalination, **147**, 411 (2002).
- [18] Ø.Hatlevik, S.K.Gade, M.K.Keeling, P.M.Thoen, A.P.Davidson, J.D.Way; Sep.Purif.Technol., **73**, 59 (2010).
- [19] M.S.Islam, M.M.Rahman, S.Ilias; Int.J.Hydrogen Energy, **37**, 3477 (2012).
- [20] T.S.Moss, N.M.Peachy, R.C.Snow, R.C.Dye; Int.J.Hydrogen Energy, **23**, 99 (1998).
- [21] S.Tosti; Int.J.Hydrogen Energy, **28**, 1445 (2003).
- [22] D.Xie, J.Yu, F.Wang, N.Zhang, W.Wang, H.Yu, F.Peng, Ah-Hyung A.Park; Int.J.Hydrogen Energy, **36**, 1014 (2011).
- [23] L.Wei, J.Yu, X.Hu, Y.Huang; Int.J.Hydrogen Energy, **37**, 13007 (2012).
- [24] E.David, J.Kopac; Int.J.Hydrogen Energy, **36**, 4498 (2011).
- [25] M.L.Mottern, W.V.Chiu, Z.T.Warchol, K.Shqau, H.Verweij; Int.J.Hydrogen Energy, **33**, 3903 (2008).
- [26] R.Sanz, J.A.Calles, D.Alique, L.Furones, S.Ordóñez, P.Marín, P.Corengia, E.Fernandez; Int.J.Hydrogen Energy, **36**, 15783 (2011).
- [27] K.Kusakabe, S.Fumio, T.Eda, M.Oda, K.Sotowa; Int.J.Hydrogen Energy, **30**, 989 (2005).
- [28] X.Hu, W.Chen, Y.Huang; Int.J.Hydrogen Energy, **35**, 7803 (2011).
- [29] M.Amanipour, E.Ganji Babakhani, A.Zamanian, M.Heidari; J.Petrol.Sci.Tech., **1**, 30 (2011).
- [30] J.Song, L.Li, X.Tan, K.Li; Int.J.Hydrogen Energy, **38**, 7904 (2013).
- [31] M.Liu, W.Sun, X.Li, S.Feng, D.Ding, D.Cheng, M.Liu, H.C.Park; Int.J.Hydrogen Energy, **38**, 14743 (2013).
- [32] J.Kim, Y.Kang, B.Kim, S.Lee, K.Hwang; Int.J.Hydrogen Energy, **36**, 10129 (2011).
- [33] Z.Zhu, L.Yan, H.Liu, W.Sun, Q.Zhang, W.Liu; Int.J.Hydrogen Energy, **37**, 12708 (2012).
- [34] T.Norby, R.Haugsrud; Dense Ceramic Membranes for Hydrogen Separation, in A.F.Sammels, M.V.Mundschau, (Eds); Nonporous Inorganic Membranes, WILEY-VCH Verlag GmbH & Co, KGaA, Weinheim (Federal Republic of Germany),

- 1-48 (2006).
- [35] S.Wang, Y.Hsu, H.Lu, C.Huang, C.Yeh; *Int.J.Hydrogen Energy*, **37**, 12548 (2012).
- [36] H.Iwahara; *Solid State Ionics*, **86-88**, 9 (1996).
- [37] T.Norby; *Solid State Ionics*, **125**, 1 (1999).
- [38] J.W.Phair, S.P.S.Badwa; *Ionics*, **12**, 103 (2006).
- [39] H.Iwahara; *Solid State Ionics*, **77**, 289 (1995).
- [40] H.Iwahara, Y.Asakura, K.Katahira, M.Tanaka; *Solid State Ionics*, **168**, 299 (2004).
- [41] Y.Huang, Q.Li, T.V.Anfimova, E.Christensen, M.Yin, J.O.Jensen, N.J.Bjerrum, W.Xing; *Int.J.Hydrogen Energy*, **38**, 2464 (2013).
- [42] Z.Zhu, W.Sun, L.Yan, W.Liu, W.Liu; *Int.J.Hydrogen Energy*, **36**, 6337 (2011).
- [43] S.Escolástico, C.Solís, J.M.Serra; *Int.J.Hydrogen Energy*, **36**, 11946 (2011).
- [44] M.Tanaka, T.Ohshima; *Fus.Engg.Des.*, **85**, 1038 (2010).
- [45] Y.Kawamura, T.Yamanishi; *Fus.Engg.Des.*, **86**, 2160 (2011).
- [46] J.Han, Z.Wen, J.Zhang, X.Xu, Z.Gu, Y.Liu; *Fus.Engg.Des.*, **85**, 2100 (2010).
- [47] H.Borland, L.Llivina, S.Colominas, J.Abellà; *Fus.Engg.Des.*, **88**, 2431 (2013).
- [48] P.Serret, S.Colominas, G.Reyes, J.Abellà; *Fus.Engg.Des.*, **86**, 2446 (2011).
- [49] Y.Kawamura, T.Arita, K.Isobe, W.Shu, T.Yamanishi; *Fus.Engg.Des.*, **83**, 625 (2008).
- [50] M.Tanaka; *Fus.Engg.Des.*, **87**, 1065 (2012).
- [51] V.Violante, A.Basile, E.Drioli; *Fus.Engg.Des.*, **22**, 257 (1993).
- [52] Y.Kawamura, M.Enoeda, T.Yamanishi, M.Nishi; *Fus.Engg.Des.*, **81**, 809 (2006).
- [53] D.Demange, S.Stämmmler, M.Kind; *Fus.Engg.Des.*, **86**, 2312 (2011).
- [54] D.Demange, C.G.Alecu, N.Bekris, O.Borisevich, B.Bornschein, S.Fischer, N.Gramlich, Z.Köllö, T.L.Le, R.Michling, F.Priester, M.Röllig, M.Schlösser, S.Stämmmler, M.Sturm, R.Wagner, S.Welte; *Fus.Engg.Des.*, **87**, 1206 (2012).
- [55] V.I.Pistunovich, A.Yu.Pigarov, A.O.Busnyuk, A.I.Livshits, M.E.Notkin, A.A.Samartsev, K.L.Borisenko, V.V.Darmogray, B.D.Ershov, L.V.Filippova, B.G.Mudugin, V.N.Odintsov, G.L.Saksagansky, D.V.Serebrennikov; *Fus.Engg.Des.*, **28**, 336 (1995).
- [56] H.Yamasaki, H.Kashimura, S.Matsuda, T.Kanazawa, T.Hanada, K.Katayama, S.Fukada, M.Nishikawa; *Fus.Engg.Des.*, **87**, 525 (2012).
- [57] R.Sacristán, G.Veredas, I.Bonjoch, I.Fernandez, G.Martín, M.Sanmartí, L.Sedano; *Fus.Engg.Des.*, **87**, 1495 (2012).
- [58] D.Demange, O.Borisevich, N.Gramlich, R.Wagner, S.Welte; *Fus.Engg.Des.*, **88**, 2396 (2013).
- [59] H.Neuberger, X.Jin, L.V.Boccaccini, B.E.Ghidersa, R.Meyder; *Fus.Engg.Des.*, **82**, 2288 (2007).
- [60] J.Wang, W.Tian, G.Su, S.Qiu, B.Xiang, G.Zhang, K.Feng; *Fus.Engg.Des.*, **88**, 33 (2013).
- [61] M.Scholz, M.Wessling, J.Balster; *Design of Membrane Modules for Gas Separations*, in E.Drioli, G.Barbieri, L.Peter, (Eds); *Membrane Engineering for the Treatment of Gases, Gas-Separation Problems with Membranes*, RSC Publishing, Cambridge (United Kingdom), **1**, 125-138 (2011).
- [62] R.W.Baker; *Membrane Technology and Applications*, 2nd Edition, John Wiley and Sons, West Sussex (England), 89-155 (2004).
- [63] A.F.Ismail, D.Rana, T.Matsuura, H.C.Foley; *Carbon-based Membranes for Separation Processes*, 1st Edition, Springer Science + Business Media; New York (NY), (2011).
- [64] S.Adhikari, S.Fernando; *Ind.Eng.Chem.Res.*, **45**, 875 (2006).
- [65] M.B.Rao, S.Sircar; *J.Membr.Sci.*, **110**, 109 (1996).
- [66] M.B.Rao, S.Sircar; *Gas Sep.Purif.*, **7**, 279 (1993).
- [67] L.Ge, L.Wang, A.Du, M.Hou, V.Rudolph, Z.Zhu; *RSC Advances*, **2**, 5329 (2012).
- [68] H.Li, Z.Song, X.Zhang, Y.Huang, S.Li, Y.Mao, H.J.Ploehn, Y.Bao, M.Yu; *Science*, **342**, 95 (2013).
- [69] S.Wang, M.Zeng, Z.Wang; *Separ.Sci.Technol.*, **31**, 2299 (1996).
- [70] J.E.Koresh, A.Soffer; *Separ.Sci.Technol.*, **22**, 973 (1987).
- [71] H.A.Meinema, R.W.J.Dirrix, H.W.Brinkman, R.A.Erpstra, J.Jekerle, P.H.Köstters; *Interceram*, **54**, 86 (2005).
- [72] S.M.Saufi, A.F.Ismail; *Carbon*, **42**, 241 (2004).
- [73] A.J.Bird, D.L.Trimm; *Carbon*, **21**, 177 (1983).
- [74] C.W.Jones, W.J.Koros; *Carbon*, **32**, 1419 (1994).
- [75] A.S.Ismail, L.I.B.David; *J.Membr.Sci.*, **193**, 1 (2001).