**Separation & Purification Reviews**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

# INNOVATIONS IN PALLADIUM MEMBRANE RESEARCH

S. N. Paglieri[a]; J. D. Way[b]
[a] Los Alamos National Laboratory, Los Alamos, NM, U.S.A. [b] Colorado School of Mines, Golden, CO, U.S.A.

**To cite this Article** Paglieri, S. N. and Way, J. D.(2002) 'INNOVATIONS IN PALLADIUM MEMBRANE RESEARCH', Separation & Purification Reviews, 31: 1, 1 — 169
**To link to this Article: DOI:** 10.1081/SPM-120006115
**URL:** http://dx.doi.org/10.1081/SPM-120006115

Marcel Dekker, Inc. • 270 Madison Avenue • New York, NY 10016

SEPARATION AND PURIFICATION METHODS, 31(1), 1–169 (2002)

# INNOVATIONS IN PALLADIUM MEMBRANE RESEARCH

**S. N. Paglieri[1,*] and J. D. Way[2]**

[1]Los Alamos National Laboratory, Los Alamos,
NM 87545, USA
[2]Colorado School of Mines, Golden, CO 80401, USA

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[*]Corresponding author. E-mail: steve.paglieri@lanl.gov

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## ABSTRACT

This review highlights various aspects of current palladium membrane research and serves as a comprehensive bibliography covering palladium membrane preparation methods and applications. There are many promising uses for palladium membranes, although widespread use of the available technologies is constrained primarily by the high cost of palladium, lack of durability due to hydrogen embrittlement, and susceptibility to fouling. Various researchers in the field are tackling these problems and fabricating thinner palladium alloy composite membranes that better withstand contaminantion and thermal cycling. What has been accomplished to address these issues and the directions presently being explored are discussed.

*Key Words*: Palladium membrane; Membrane reactor; Alloy; Hydrogen diffusion

## 1. INTRODUCTION AND BACKGROUND

Hydrogen separating membranes made of palladium alloys have been developed over the past 50 years into a technology that in some instances is used in practice. Illustrations include the ultra-purification of hydrogen for use in semiconductor manufacturing processes, and hydrogen generators for remote or small-scale usage.[1–9] Areas presently being researched include membrane reactors to supply hydrogen gas for fuel cells or the chemical process industry. Palladium membranes have other important technological ramifications as well. They can produce hydrogen gas with ppb impurity levels for analytical instruments, for hydrogen leaks into (or removal from) vacuum systems, or deposition processes in the computer and aerospace industries.[5,10–17] Palladium-alloy diffusers are a key component in processes that recover the radioisotopes of hydrogen that are used and produced in nuclear fission and fusion reactors.[18–28] The following sections contain important background information on palladium membranes, discussion of state-of-the-art fabrication methods, and some details of how the technology may be applied.

A host of reviews detail the potential uses of palladium membranes in membrane reactors and hydrogen recovery.[29–70] There is a wealth of information on palladium membranes found in patents.[71–76] Many of the science and engineering aspects of metal membranes and membrane reactors have formerly been well covered. Though there is an attempt here to avoid redundancy, some topics addressed previously are defined here for the sake of completeness, to elaborate on certain points, and to cite the latest publications. In addition to an overview of palladium membrane development and uses, the focus at hand will be on the problems that remain to be overcome and what is being done or what should be done to resolve them. Some of the interesting questions related to the technology will be dealt with. For example, what is the precise influence of grainsize on hydrogen permeability through palladium? The relationship between preparation methods and mechanical stability, as well as other issues affecting high temperature membrane performance will be discussed.

Pure hydrogen is a valuable industrial material and is consumed on the order of billions of cubic meters per year.[70] Hydrogen, produced primarily by steam reforming of hydrocarbons like natural gas, is used for hydrogenations in the chemical process industry, iron ore reduction, as a blanket gas for brazing, during the sintering and annealing of metals to prevent oxidation and nitriding, as a fuel, as a coolant for power station alternators and generators, and as a carrier gas during the doping of silicon wafers or chemical vapor deposition (CVD) in the semiconductor industry.[5,9,52,77–84] Presently, a major hydrogen sink is the hydrodesulfurization of fuels.[79,85] It is also used in scientific and military balloons and as a rocket fuel.[78,86,87]

Separations account for a large fraction of energy expenditure and capital investment in the chemical process industry. Common technologies used for separating hydrogen consist of solvent absorption, pressure swing adsorption (PSA), cryogenic recovery, and polymer membranes.[45,79,88–91] Polymer membranes currently compete with the other technologies to reduce the hydrogen/carbon monoxide ratio in synthesis gas (syngas), or to recover hydrogen from purge or offgas streams in ammonia or petrochemical plants.[43,52,90,92–95] Polymer membranes are economical in some applications, although the higher temperatures of most chemical reactions and many waste gas streams precludes their use, at least without process modifications such as cooling prior to introduction to the membrane. Typically comprised of hollow fiber modules of various kinds of polymers (such as polyimide), hydrogen separating polymer membranes can be made very thin but are generally confined to use at temperatures below 150°C.[96–99] In general, membrane systems typically require lower capital investment although their main liability is that recompression of the permeated hydrogen is usually required.[43,88]

Inorganic membranes are increasingly being utilized to separate gas mixtures. Some gases preferentially permeate through certain metals, enabling a permselective (dominant permeation of one species) dense metal membrane to be formed. For example, hydrogen exclusively permeates through palladium while oxygen permeates through silver.[100–114] This review focuses solely on hydrogen separating metal membranes. Meanwhile, the fabrication and characterization of porous membrane materials has also been heavily researched in the past decade. Various materials, particularly those produced from alumina ceramics have been thoroughly scrutinized. Zeolites or silicalite films, with their well-defined pore sizes, have been studied for use as hydrogen permselective molecular sieving membranes.[49,115–122]

The properties of palladium are now taken advantage of as the basis for some high sensitivity hydrogen sensors,[123–125] and palladium sometimes serves as a catalyst or membrane electrode in fuel cells.[126–136] Since palladium is endowed with excellent catalytic properties it is a quintessential ingredient in catalysts for the chemical industry and in automotive catalytic converters. As a platinum group metal, its inert nature and good conductivity has enabled the replacement of some gold microcircuit components with palladium alloys.[137] Palladium is also purported to enable the nuclear process of cold fusion.[138]

In 1863, Sainte-Claire Deville and Troost discovered that hydrogen permeates through palladium and then in 1866, Graham discovered the capacity of palladium to absorb several times its volume of hydrogen at room temperature.[139–141] The implication that palladium occludes hydrogen was later exploited by Zelinskii at Moscow University,[58] and by Snelling who formed hydrogen separating palladium septa circa 1916.[142] While palladium was used in laboratories as early as the 1920's to obtain high-purity hydrogen, apparently, palladium membranes did not receive much commercial attention until several companies (such as Atlantic Refining Company, Milton Roy Co., J. Bishop and Co., Johnson Matthey Metals, Engelhard Industries, Inc., and Union Carbide) began using palladium membrane technology to generate hydrogen beginning in the late 1950's.[5,45,80,83,91,135,141,143–153] Since then, small-scale palladium membrane modules have conveniently produced high-purity hydrogen at remote sites and for industrial, laboratory, or military purposes.[5,82,154,155]

One of the most promising applications of palladium membrane technology is as a membrane reactor where chemical reaction and product purification by separation occur simultaneously. Chemical reactions can be carried out more efficiently in hydrogen separating membrane reactors. By removing product from the reactor, in this case hydrogen, thermodynamically limited reactions can be driven towards completion, significantly enhancing conversion over the theoretical equilibrium conversion based on the composition of the reactor feed stream.[156–158] Additionally, pure hydrogen recovered on the permeate side of the membrane can be utilized for other purposes. Conversely, adding hydrogen along the length of a reactor can favorably enhance hydrogenation product yields.

Palladium membranes are capable of operating at much higher temperatures than polymer membranes, making them ideal for use as a membrane reactor or for extracting hydrogen from high temperature gas streams. Gryaznov, Pfefferle, and Wood initiated groundbreaking membrane reactor investigations where palladium membranes were used to add or remove hydrogen from a reaction space resulting in increased yield and catalyst effectiveness.[4,159–165] Palladium membranes are ideal for hydrogenation/dehydrogenation reactions due to excellent control over hydrogen delivery or removal from the reaction zone.[58] Ideally, an endothermic dehydrogenation and an exothermic hydrogenation would be coupled or ''conjugated'' where each reaction takes place on opposite sides of the membrane packed with catalyst.4,49,58,162–164,166–171] Thus, hydrogen and heat would be transferred most effectively, as two products form and energy is supplied directly where it is needed.

By either adding or removing hydrogen to drive equilibrium restricted reactions to the desired product side, reactor volume and temperature may be lowered, fewer undesirable byproducts form through side reactions, and less unreacted feed must be recycled, saving on downstream separation requirements, equipment size, and energy usage.[4,157,172–178] Accordingly, a robust hydrogen permselective membrane has the potential to change the chemical industry by replacing traditional reaction and separation procedures. This could result in sizable savings in energy consumption and capital investment in equipment. Minimizing reactor surface-to-volume ratio can be advantageous in certain situations, for example, in a portable fuel reformer generating hydrogen for consumption in a fuel cell that provides electricity for vehicle propulsion (see page 66).

Although the notion of a hydrogen separator based on palladium metal has been around for more than a century, research centering on the development of technologically and economically feasible hydrogen separating membranes based on palladium skyrocketed in the last decade. In early work in the United States and former Soviet Union, relatively thick-walled tubes were employed. Up to the 1980's, banks of membranes were comprised of palladium alloy tubes and capillaries with wall thicknesses of at least 100 μm for structural integrity. The nearly perfect hydrogen permselectivity of thicker palladium membranes enables them to provide very high purity hydrogen for use in the semiconductor manufacturing industry or for recovering hydrogen isotopes. Unfortunately, the cost of monolithic palladium foils and tubes is prohibitive for most purposes. So, in order to produce a reliable and economical means of hydrogen separation on an industrial scale, a thin ($<20$ μm thick), adherent, nonporous, and durable palladium film must be applied to a hydrogen-permeable support.[144] Kikuchi and Uemiya were the first to publish a large amount of work on palladium composites that used porous membranes as supports.[173,179–188] Over the last decade, composite palladium membranes that couple high permselectivity with reasonable hydrogen flux have been fabricated by many researchers using a range of deposition methods and supports.[189]

Many different membrane configurations have been developed in the attempt to minimize palladium film thickness while maintaining membrane integrity and high hydrogen flux.[52,93] Composite membranes consist of a thin layer of palladium on a hydrogen permeable support so that palladium films with micron thicknesses or less are readily attainable. Very high hydrogen permselectivity is possible if a defect-free palladium film can be deposited onto the membrane support and a leak-free seal can be made between the inlet and outlet connections and the composite membrane. In addition, the membrane can be operated at high transmembrane pressure differentials because the substrate provides mechanical support for the thin palladium film.

Hydrogen is costly to produce or to separate from gas mixtures such as reactor effluent or waste streams due to the high capital and energy expenditures associated with compression, heat exchange, cryogenic distillation, and PSA. An affordable, tough, and selective hydrogen separating membrane could significantly reduce these costs, and ultimately replace traditional unit operations or be integrated into an existing process to recover hydrogen. Recovery of hydrogen from waste gas or purge streams (such as hydrotreater off-gas) is a potentially large application of palladium membrane technology.[6] Such streams are typically flared or combusted as fuel gas to provide heat for other processes, annually consuming up to 2.5 trillion standard-cubic-feet of valuable hydrogen.[90] Coal gasification or natural gas reforming combined with a palladium membrane reactor could become a tremendous source of hydrogen.[93,190–194] Steam reforming, particularly of methanol, is frequently the source of hydrogen for small-scale hydrogen generating membrane units.[9,80,93,195,196] Production of pure hydrogen for fuel cell use could be another important function of a palladium membrane reactor.[184] Using methanol powered fuel cell vehicles in the U.S. could conserve 2–4 million of barrels of oil per day through increased efficiency over the internal combustion engine.[197]

However, to be commercially viable, a membrane must possess high flux and hydrogen permselectivity over a lifetime of years under process conditions, in addition to being cost effective. A major shortcoming of palladium as a membrane material is the high and fluctuating cost of this precious commodity metal and the difficulty of fabricating defect free membranes with palladium films on the order of microns or less. The use of palladium must be restricted not only due to its high cost, but to maximize the flux through the metal since permeability is inversely proportional to palladium film thickness. For example, in order to begin to compete with state-of-the-art industrial methane steam reforming, it has been estimated that a palladium membrane around 2 μm thick must be used.[88] Therefore, reducing palladium use in membrane fabrication has been a foremost consideration. Then again, it should be noted that the palladium in diffusion modules can be reclaimed and refabricated.[135]

There are other characteristics of pure palladium that impede the use of palladium membrane technology. These problems have been thoroughly studied but in most cases acceptable solutions have not yet been found. Long-term stability at high temperatures (>450°C) has been a problem, mainly deactivation by carbon under reaction conditions in a membrane reactor.[117,198–200] Additionally, pure palladium may undergo a phase transition ($\alpha \rightarrow \beta$) in the presence of hydrogen at temperatures below 300°C, corresponding to an increase in lattice size as it absorbs hydrogen, leading to warping and embrittlement.[141,201–205] This effect can be avoided by alloying palladium to lower the critical temperature, $T_c(\alpha, \beta)$, for the coexistence of the $\alpha$ and $\beta$ phases.[45,206,207] Silver, ruthenium, copper and other elements achieve this at specific concentrations while maintaining hydrogen permeabilities comparable to or greater than pure palladium.[30,145,146,208–213] Palladium is also susceptible to contamination or irreversible poisoning by common constituents of industrial streams such as sulfur.[214]

For a palladium membrane system to replace a conventional practice and be accepted by industry, it must meet the following criteria: minimal palladium thickness; high permselectivity for hydrogen; high output per unit volume; steady and predictable performance over a long period of time at high temperature and pressure; adaptability to a variety of high temperature separation and membrane reactor applications; resistance to poisoning by hydrogen sulfide, chlorine, carbon monoxide, and hydrocarbons; and the ability to withstand thermal cycling.[40,64,65] Despite the above hurdles, the capability of palladium alloys to selectively diffuse hydrogen while resisting permanent contamination nevertheless makes it an excellent candidate for large-scale hydrogen separating membranes. Supported palladium or palladium alloy thin film membranes have already been demonstrated to be a suitable choice of technology with respect to separation factor and high hydrogen throughput.

A formidable volume of work has been conducted on palladium membrane reactors and palladium membranes for separating hydrogen. An understanding of the theoretical aspects associated with palladium membrane manufacture and use such as hydrogen diffusion in metals and metal deposition processes is essential in developing an effective membrane configuration. The theory of hydrogen permeation in palladium is outlined in this light. Several reviews are available[57,201,202,215] while the pertinent background information is covered in this report.

## 1.1 Permeation of Hydrogen Through Metal Membranes

The importance of the palladium/hydrogen system has prompted many studies and while the permeation of hydrogen through metals has been thoroughly described previously, it is revisited here as a foundation for further discussion. Permeability, $P$ (mol/m·Pa·s), of hydrogen through a metal is a function of diffusivity, $D$ (m$^2$/s), and solubility, $S$ (mol/m$^3$·Pa$^{0.5}$):[57,216,217]

$$P = D \cdot S \equiv (\mathrm{mol} \cdot \mathrm{m}/\mathrm{m}^2 \cdot \mathrm{s} \cdot \mathrm{Pa}^{0.5})$$

The addition of other metals to palladium often decreases one property but increases the other so that the net result is increased hydrogen permeability.[91,206,218–222] Palladium is very permeable to hydrogen but essentially impermeable to other gases, so at least in theory, perfect permselectivity can be attained. In practice, purity is limited to tens of ppb due to small amounts of carbon and other impurities that diffuse through the metal lattice and grain boundaries.[3,7,13,91,223–227] Many different sample preparation methods and permeation measuring techniques have been employed to determine the hydrogen permeability of metals.[201,202,228–234]

Diffusion takes place because of an activity gradient or difference in chemical potential.[235] This is usually caused by a difference in hydrogen partial pressure across the metal. Hydrogen permeates through solid metals via what is termed a solution-diffusion mechanism, involving the following steps:[214,236–241] diffusion through the boundary layer to the metal surface from the gas; dissociative chemisorption (diatomic hydrogen molecules adsorb on the metal surface and are separated into atomic hydrogen),[242]

$$H_{2(g)} \leftrightarrow 2H_{(chemisorbed)};$$

absorption into the bulk metal; diffusion to the opposite face through the metal lattice; passage from the bulk to the surface; associative desorption (recombination into molecular hydrogen); and diffusion away from the surface into the gas.[215,243] Each process can be described by a forward and reverse rate, for example the dissociative chemisorption of hydrogen,[244–249]

$$H_{2(gas)} \underset{k_2 c_H^2}{\overset{k_1 p_H}{\longleftrightarrow}} 2H_{(surface)}$$

where $k_1$ and $k_2$ are the rate constants for adsorption and desorption respectively, $p_H$ is the partial pressure of hydrogen, and $c$ (mol/m$^3$), is concentration of hydrogen in the metal. The overall permeation process is influenced by the metal surface roughness, purity, annealing history, and surface cleanliness.[215]

Assuming equilibrium between the hydrogen molecules in the gas phase and hydrogen atoms at the gas/solid interface, the concentration of atomic hydrogen just within the metal, $c_H$ (mol/m$^3$), is proportional to the square root of hydrogen pressure (Sieverts' law),[91]

$$c_H = K_s p_H^n \equiv (\mathrm{mol/m^3})$$

where, $K_S$ (mol/m$^3 \cdot$ Pa$^{0.5}$), is Sieverts' constant and $p_H$ (Pa) is the partial pressure of hydrogen in the gas phase.[91,247,250–257] Solubility of atomic hydrogen in the lattice is described by Sieverts' constant assuming dilute solution and minimal interaction between hydrogen atoms.[258] Hydrogen solubility decreases with increasing temperature. The power dependency, $n$, is 0.5 because hydrogen diffuses through the metal in the atomic form.[259] This square-root dependence of solubility on pressure is known as Sieverts' law. At low temperature ($<150$°C) and at higher pressures (>100 Torr) there can be significant departure from this relationship (at higher hydrogen contents).[215,260,261]

At lower temperatures and pressures ($<10^3$ Pa) the slow rate of desorption (recombination reaction) from the low-pressure side can hamper flux, while adsorption-limited flux is encountered at very low hydrogen partial pressure on the input side or from excessive contamination.[113,238,241,248,262–266] The effect of surface conditions on permeation is even more evident with thin films where dissociation and adsorption of hydrogen on the surface can become the rate-controlling step for permeation through the metal.

External mass transfer resistance, likely to be encountered on the low-pressure side of the membrane, can also reduce the hydrogen permeation rate.[238,267–269] This is particularly true for very thin membranes ($<10$ μm) supported on porous supports that offer substantial mass transport resistance.[238,270–272] Consequently, $n$ may vary between 0.5 and 1 for composite membranes.[269,270,273] With high rates of hydrogen permeation through a membrane, concentration polarization or a hydrogen partial pressure gradient can reduce flux.[274,275] Also, as the metal film becomes thinner, flux tends to become independent of thickness, i.e. surface processes become rate controlling.[276,277] Percent recovery or operation efficiency will then depend on factors such as the hydrogen partial pressure in the feed, and bleed and sweep (if used) gas flowrates.[2,5,135,144,145,250,278 – 283]

The surface roughness factor, $\sigma_s$, is a notable parameter in hydrogen adsorption and desorption.[58,239,241,284–286] The rate of hydrogen uptake is faster at higher effective metal surface area, perhaps because of a reduction in activation energy for both the dissociation and recombination of molecular hydrogen as well as an increase in the number of active sites.[215] Application of a palladium or platinum layer consisting of very small metal particles to reduce the kinetic limitations of the hydrogen adsorption process is a common practice in electrochemistry and palladium membranes have been activated in this manner as well.[221,287–289] Etching can also increase the membrane surface area.[290,291] Thermally diffusing zinc, copper, or mercury into a palladium-alloy membrane and then chemically removing it has increased the catalytic surface area and increased the rate of hydrogen dissolution into the membrane.[44,58,292–295] Methods exist for either gas phase or electrochemical determination of roughness factor or true surface area.[296]

There is ongoing debate over the thickness of palladium film at which surface processes become influential in determining the rate of hydrogen permeability.[297] Hydrogen flux will be rate limited by either bulk diffusion or the dissociation or recombination kinetics (surface processes).[38,215,298–301] A detailed model of the permeation process through palladium was constructed by Ward et al. using rate equations (based on the literature) for each step of the permeation process.[238] Their results identified that for temperatures above 300°C and palladium films as thin as 1 μm, diffusion through the bulk metal is the rate-limiting step. This is fairly consistent with the results of other researchers[185,259] although Criscuoli et al. estimated that below 10 μm of palladium the influence of surface processes becomes significant.[302]

Hydrogen is in both the molecular and atomic form on the surface and exists inside the metal in the atomic state so that the value of $n = 0.5$ when bulk diffusion is the rate controlling step for permeation.[214,303] The value of $n$ is very sensitive to the permeability measurement and Sieverts' relationship may not be followed for several reasons.[135,144,304–307] When hydrogen dissociation or associative desorption replaces bulk diffusion processes as permeation rate controlling (at lower temperatures and pressures), due to the presence of contaminants for instance or when the membrane is very thin, $n$ has a higher value.[40,244,249,265,277,308–311]

Palladium is one of the most efficient metals for hydrogen adsorption, dissociation and recombination despite being an order of magnitude less permeable than some of the refractory metals such as tantalum, vanadium and niobium.[6,99,312] On the other hand, these metals are less reactive for the dissociation of hydrogen into its atomic form and are unable to rapidly absorb hydrogen due to passivation by oxygen and other impurities.[313–320] Hence, a palladium film is required on both sides of a refractory metal foil as a noble metal protective layer as well as a means for dissociating and recombining hydrogen.[6,193,197,227,253,309,321–342]

Knudsen diffusion dominates when the mean free path of the molecule or atom is greater than the pore diameter.[270,343,344] Then collisions with the pore wall are of the same frequency as intermolecular collisions and the permselectivity is determined by the ratio of the reciprocal square root of molecular weight:[345,346]

$$\alpha_{Kn} = \sqrt{MW_2}\Big/\sqrt{MW_1} .$$

Here, $\alpha_{Kn}$ is the Knudsen separation factor and $MW_1$ and $MW_2$ are the molar masses of the lighter and heavier species respectively. Except in some special cases (uranium enrichment for example) membranes with only Knudsen permselectivity are generally not used industrially for gas separations.[347]

The contribution of modes of diffusion such as Knudsen or viscous flow through defects or microcracks in the metal will also increase $n$.[215,346] Diffusion of molecular hydrogen along grain boundaries or via surface diffusion is proportional to $p_H$ instead of $p_H^{0.5}$.[263,348] Other reasons for deviation of permeation from half-power pressure dependency include changes in structure, contamination, or stress in the metal induced by either hydrogen adsorption or heat treatment.[349–355] Surface impurities reduce the sticking coefficient and increase the activation energy for dissociative chemisorption of hydrogen so that dissociation (or recombination on the downstream side) becomes the rate-limiting step for permeation.[311,356–358]

In general, surface effects can be neglected and bulk diffusion is the rate controlling process for permeation through a metal membrane. Once inside the metal, Fick's first law may be used to describe the steady-state permeation rate or flux of hydrogen through the solid:[343]

$$J = -D\frac{dc}{dx} \equiv (\mathrm{mol/m^2 \cdot s}).$$

Substituting in the relationship for hydrogen concentration in the metal (Sieverts' law),[215] and assuming a homogeneous solid and low hydrogen concentration (so that $D$ is independent of hydrogen concentration) and integrating, results in:

$$J = \frac{P}{l}(p_{H,1}^n - p_{H,2}^n) \equiv (\mathrm{mol/m^2} \cdot s)$$

where $P$ is the permeability ($\mathrm{mol{\cdot}m/m^2{\cdot}s{\cdot}Pa}^n$), $l$ (m) is the membrane thickness, and $p_{H,1}$ and $p_{H,2}$ (Pa) are the partial pressures of hydrogen on the feed and permeate side respectively. Through nonlinear regression, the values of $n$, $P$ and the apparent activation energy, $E$ (kJ/mol), can be obtained if flux data is taken at different temperatures and pressures.[270,273] By plotting permeance ($P/l$) vs. 1000/T (where T is the temperature in K), the apparent activation energy for hydrogen diffusion through the metal can be determined through this Arrhenius relationship.[273,304,359,360] If the film contains defects (the permselectivity is not perfect), they should be accounted for by subtracting their contribution to flux when calculating the true hydrogen flux through the metal film itself. Otherwise, the flux value will be higher than actual.

Inside the metal, hydrogen occupies octahedral interstices and exists as an electronically screened proton enveloped by a cloud of semi-bound electrons.[40,202,258,361–364] Hydrogen electrons partially enter the unfilled d-band of the metal.[220,247,365,366] The pathway for hydrogen diffusion with the lowest energy is from one fcc interstitial octahedral site to another, probably by diffusion through a tetrahedral site with local lattice deformation.[362,367–370]

While suitable for accurately depicting hydrogen diffusion in most cases, the above representation of hydrogen diffusion based on Fick's law may be too simplistic for precise modeling, especially of nanocrystalline or amorphous materials.[235,371,372] Hydrogen diffusivity and solubility will change with stress and strain induced by hydrogen absorption producing a nonlinear hydrogen concentration profile.[353,373–377] In fact, to a certain degree the diffusion coefficient increases with hydrogen concentration and hydrogen can permeate against the hydrogen concentration gradient along lines of strain.[235,289,378–393] This has been termed uphill diffusion and it is less pronounced at higher temperatures.[378] It is important to consider this effect when estimating diffusion coefficients as it reduces the steady state flux. The contribution of the negative hydrogen flux vector created by strain gradients may be negligible at the high temperatures at which membranes typically operate.[394–396]

In reality, a metal composite membrane on a porous support may contain microcracks or pinholes that affect the mass transfer through it. So, it should be considered that transport is a combination of atomic diffusion through the metal (solution–diffusion), surface diffusion, molecular sieving, capillary condensation, Knudsen diffusion, ordinary or Fickian diffusion, and viscous (bulk or Poisseuille) flow through the metal film, the porous support, and defects in the metal film or membrane seals.[35,117,199,276,397–412] Furthermore, a porous or semi-permeable support will often significantly lower the hydrogen permeability of the composite membrane whether or not the palladium coating is continuous.[271]

The permeance of gases other than hydrogen can be quantified by considering the contributions from Knudsen diffusion, ordinary or bulk diffusion, and viscous flow.[402,413] Quantification of the contribution of defects in the palladium film to hydrogen permeation through a composite membrane can be carried out by measuring the hydrogen and inert gas fluxes through both the composite membrane and the porous support itself. To calculate the fraction of porous substrate not covered with palladium, the flux of inert gas through the defects in the composite membrane (or leaks through the seal) can be compared to the inert gas flux through the uncoated support. The hydrogen fluxes through the palladium film and the defects can be estimated by using model equations for diffusion through the porous support and the palladium (see for example Schramm and Seidel-Morgenstern).[414]

The sort of diffusion through defects in the palladium film or in the sealing material can be determined by conducting permeation experiments with inert gases. The flux ratio of two different permeating gases (other than hydrogen) will reveal the size of the pores by how near the value is to the Knudsen separation factor.[415] Thus, the amount of hydrogen leaking through the defects in the metal film can be projected and subtracted from flux measurements to estimate the actual amount of hydrogen permeating through the metal film itself.[276] The adjusted values should be used to calculate the permeance from a plot of flux vs. $p^{0.5}$. A straight line should be formed and the deviation of the intercept from the origin will be an indication of data accuracy.[215,416] For estimation of pore size using the flux of gases other than hydrogen, see Mardilovich et al.[304]

Surface diffusion or spillover may play an important role in the dissociation and diffusion of hydrogen through composite metal membranes.[348,400,408,410,411,413,417,420] In this mechanism, atomic hydrogen is chemisorbed and transported on the surface of the metal film or particles.[345,421–425] Analogously, discontinuous platinum or rhodium films deposited onto the surface of metal foils increase the absorption and permeation rate.[288] In this case, the metal granules act by dissociating molecular hydrogen into atomic hydrogen that spills over onto the palladium surface and is more readily absorbed.[426] Platinum group metals inside the pores of a membrane support can also transport atomic hydrogen by surface diffusion, resulting in separation factors much greater than those obtained from Knudsen diffusion.[400,408,417,427–430] The specific contribution of this form of transport through membranes has been qualitatively observed but remains to be quantified.

### 1.1.1 Permeability Measurement

Before a membrane can be tested for permeability, it must be sealed into a permeation apparatus. This is often one of the most difficult and critical aspects of membrane technology. Metal foils, tubes, and porous metal substrates can often be brazed or welded relatively easily or sealed into a fitting with a soft metal ferrule.[431–433] Metal gaskets (such as copper or aluminum) are frequently used to seal flat membranes into a permeation cell using a knife-edge or through diffusion bonding by heating at a high enough temperature so that the gasket and membrane interdiffuse.[354,434,435] With brittle ceramic composite membranes however, more complicated solutions are required.

The most obvious solution to sealing problems is to keep the seal out of the heated zone. While this may be possible in the laboratory it is impractical for an industrial module. Obtaining a gas-tight seal at high temperatures and pressures with interfaces between metals and porous ceramics or glass is nontrivial. The face to be sealed must not leak or else gas will bypass the selective metal layer and lower the hydrogen permselectivity. Sealing porous ceramics is usually accomplished with high temperature glaze. O-rings, ferrules, or gaskets made of graphite are often employed in compression fittings due to their softness and high temperature stability. With graphite, operation in an oxidizing atmosphere up to 450°C is permissible and operation in reducing conditions up to much higher temperatures is possible. Defects in a membrane may often be found at the ends where there is an interface between the glazed region and the palladium film. Quicker et al. overcame this problem by slicing and polishing the faces of the composite membrane after palladium deposition and using graphite seals.[436]

Alternative membrane sealing methods include cermet (ceramic–metal) technology.[64] Porous ceramic supports can be infiltrated with a metal/metal oxide that strengthens the ceramic and permits brazing to a metal fitting.[437] With alumina, strong cohesion is obtained through interfacial compounds such as $Cu/Cu_2O/CuAlO_2$.[438] It is important to obtain good adhesion and wetting between the metal and ceramic as well as pay attention to the coefficients of thermal expansion of the cermet and the metal fitting. Gryaznov et al. sintered a porous ceramic membrane support with stainless steel gaskets around its edge that had a matching coefficient of thermal expansion.[62]

During start up and shut down, the palladium membrane should be purged with inert gas to avoid hydrogen embrittlement.[93,439] Permeability is often measured with single gases rather than mixtures. In this case, the ratio of hydrogen flux to that of another gas yields the ideal separation factor, $\alpha'$, or permselectivity:[304,440]

$$\alpha'_{i/j} = \frac{J_i}{J_j}.$$

Measuring the concentration of species in the permeate when mixed gas streams are used enables the calculation of separation factor:[441]

$$\alpha_{i/j} = \frac{(C_i/C_j)_{permeate}}{(C_i/C_j)_{feed}}.$$

There is very little evidence that mixed gas permselectivity (separation factor) differs from ideal separation factor with palladium membranes. The possibility has been suggested that hydrogen increases separation factor by swelling the lattice and constricting grain boundary space where other gases may diffuse.[442] However, hydrogen has also been shown to facilitate the copermeation of some other gases through metal.[3,223–225] For example, to obtain ultrahigh purity hydrogen (low ppb impurities) through a palladium membrane, a methanator for converting carbon monoxide and carbon dioxide to methane is required.[3] Methane is stable at the temperature of purifier operation (350–450°C) while carbon monoxide and carbon dioxide can dissociate and the carbon diffuses through the palladium (facilitated by hydrogen), forming methane on the downstream side with permeated hydrogen.[225]

It is important to purge the apparatus thoroughly after hydrogen permeation experiments and before measurement of non-hydrogen gases. Otherwise back permeation of hydrogen can actually result in a negative flux through the membrane for some period of time and this will result in a larger apparent separation factor.[304]

### 1.1.2 Effects of Contamination

The presence of surface contamination inhibits the hydrogen dissociation and recombination reactions and thus the observed permeability.[377,443–445] Contaminants include sulfur compounds, chlorine, carbon, carbon monoxide, ammonia, and some metals.[199,200,214,259,301,306,443,446–457] When processing hydrocarbons, sulfur species such as hydrogen sulfide and heterocyclic compounds like thiophene are commonplace in many hydrocarbon streams. Sulfur and carbon can also segregate to the palladium surface from within the metal at high temperatures, impeding hydrogen uptake.[200] Hydrocarbons inhibit permeability by either adsorbing on the surface or reacting to form carbonaceous layers at higher temperatures.[226,458,459] The degree of these effects will vary with palladium alloy composition. While hydrocarbon contamination may usually be removed it can permanently change the membrane structure.[198–200,460,461]

Chemisorbed surface species raise the energy barrier between the adsorbed and subsurface hydrogen states as well as geometrically block adsorption sites, interfering with hydrogen dissociation.[215,301,459,462–468] For example, at coverages as low as 0.18 monolayer, carbon monoxide raises both the hydrogen desorption energy and the activation energy for dissociation on the surface.[466] One impurity atom may block multiple hydrogen adsorption sites.[311,469] Small amounts of contamination on *either* the upstream or downstream surface of the membrane can significantly reduce permeation flux through the membrane.[263,306] In most cases, poisoning is reversible by treatment in air, steam or hydrogen.[445,470,471]

Coating or replacing the palladium film with a more noble metal such as platinum has successfully protected membranes from hydrogen flux reduction due to the formation of impermeable sulfur compounds on palladium at high temperature.[193,449,450,472] However, platinum is an order of magnitude less permeable than palladium to hydrogen.[237] Palladium membranes are destroyed by sulfur because of a large lattice expansion while the lattice constant of platinum sulfide is only slightly different from that of the pure metal.[428,429] Platinum sulfidation is more significant at lower temperatures. Furthermore, the hydrogen flux through the platinum membrane prior to sulfidation can be partially recovered by oxygen treatment.[428]

Palladium readily catalyzes the polymerization of hydrocarbons and they can collect on the surface, inhibiting permeability.[226,473] Exposure to unsaturated hydrocarbons, alcohols, or carbon monoxide amplifies this problem, mainly under reaction conditions. Oil from a vacuum pump is another potential source of carbon.[445] Deposited carbon can diffuse into the metal (facilitated by hydrogen), and a supersaturated solid solution of up to 13 atom % can form under the right conditions.[226,301,458,474–477] Filamentous carbon can also be formed on the membrane surface.[461] A layer of silica or titania on the surface of the palladium membrane may reduce carbon formation.[478,479]

Chabot et al. found that carbon dioxide and methane had limited effect on the hydrogen permeation rate through a palladium membrane, while Chen et al. observed a 10% reduction in flux in the presence of $CH_4$ or $C_2H_4$. In the latter scenario there was no carbon buildup so hydrogen flux reduction was due to chemisorbed impurity molecules interfering with the hydrogen dissociation process. Unsaturated hydrocarbons seem to be especially troublesome. For example, propylene polymerizes especially easily, fouling the membrane surface above 500°C.[117,199,459,480–482] Carbon can destroy the membrane, presumably by diffusing into it or causing it to delaminate from the support through the formation of a supersaturated solid solution.[117,199,226,474,480] The exact mechanism for this phenomenon is unclear, although it may include the participation of a mobile carbon/palladium entity.[200,482,483] Moreover, morphology changes (fracturing and pitting) have been observed during the hydrogenation of ethylene at 150–200°C.[200] A thin ($<0.5$ μm) layer of sol-gel titania ($TiO_2$) coated on the membrane stopped the destruction by forming a layer for hydrocarbon adsorption and reaction with spillover hydrogen from the membrane.

Exposure of the membrane to certain metallic vapors or chlorine compounds can irreversibly poison palladium, severely decreasing hydrogen permeability.[306,443] Mercury from a diffusion pump or metals volatilized during thermal treatment of a catalyst can permanently reduce the hydrogen permeability of a membrane by adsorbing and diffusing into the palladium.[135,259,448,484] Mercury can actually cause membrane corrosion.[432,485,486] To regenerate a membrane poisoned with chlorine, steam has been effective.[443]

### 1.1.3 Air Treatment

Air or oxygen exposure followed by hydrogen reduction increases the hydrogen permeability of palladium by increasing the surface area and removing contaminants that inhibit hydrogen dissociation.[215,361,487–490] Oxygen treatment may increase the surface area by creating palladium oxide that is then reduced, raising the activity or number of sites for hydrogen dissociation, thereby increasing the rate of hydrogen uptake.[40,288,305,306,491–500] Supported palladium catalysts have been observed to undergo redispersion upon redox treatment (at 450–500°C) and sintering in pure hydrogen (500 or 600°C).[501]

Many researchers treat palladium membranes with air as a routine procedure for reactivation.[416,443,502–504] Either air or hydrogen treatments have resulted in an increased catalytic activity and hydrogen permeability, possibly due to decarburization.[359] Cycles of adsorption and desorption of hydrogen may have an effect similar to oxygen exposure. Periodically reversing hydrogen flow through the membrane (backflushing) also helps to restore flux.[6,40] Hydrogen itself may also reconstruct the surface.[505] Another explanation for the increased permeability is that the removal of impurities such as carbon that have segregated to grain boundaries leaves micropores.[226]

### 1.1.4 Influence of Microstructure on Hydrogen Permeability

The metal microstructure influences permeability as well.[238,327] Diffusivity may be greater through nanostructured materials (grainsize < 50 nm) that have a high volume fraction of grain boundaries (intercrystalline space) than through polycrystalline metal foils.[506–508] In some cases, short-circuit grain boundary diffusion increased the hydrogen permeability through nanocrystalline palladium.[509–513] Some researchers have found that a high fraction of grain boundaries, dislocations, vacancies, and voids actually offer increased resistance to hydrogen permeation.[469] Heinze et al. found that diffusion in the bulk of $PdAg_{23}$ (grainsize>100 nm) was faster than grain boundary diffusion (grainsize < 40 nm).[514] This result was attributed to impurities in the metal that segregated at the grain boundaries acting as hydrogen traps. Nanocrystalline nickel has been found to have higher hydrogen permeability due to grain boundary diffusion of hydrogen.[515–517]

Lattice defects, grain boundaries, and microvoids probably act as traps, slowing hydrogen permeation and increasing the activation energy for diffusion.[518–520] Cold working that introduces lattice defects through deformation creates traps (such as dislocations) that increase the solubility (at low hydrogen concentration) but reduce the diffusivity of hydrogen in the metal although increased diffusivity is observed when these traps become filled.[229,521–532] The $\alpha \longleftrightarrow \beta$ transformation also causes deformation and microstrain that creates dislocations so hydrogen solubility is increased.[229,520,533–543] Kagan et al. saw that thermal cycling in the presence of hydrogen caused internal hardening that reduced hydrogen permeability[543] while Bucur et al. measured decreased diffusivities and increased solubilities in palladium and $PdAg_{23}$ samples containing defects.[544]

Metal films deposited by different techniques can be expected to possess varying permeability characteristics. Thin palladium films deposited on iron by RF sputtering (0.68 and 1.36 μm thick) and electron beam (e-beam) evaporation (22–135 nm thick) were found to have hydrogen diffusivities approximately 2 orders of magnitude lower than in bulk palladium because of their structure, specifically the large number of lattice defects and grain boundaries.[318] Kajiwara et al. deduced that smaller grains deposited by organometallic chemical vapor deposition (MOCVD) had higher flux because of the large effective area for surface diffusion through the metal film.[428–430,545] This is in contrast to the work of Lin and coworkers who observed the opposite relationship (larger hydrogen permeance with increasing grainsize) with films deposited similarly.[409,442] This was ascribed to the film microstructure. Furthermore, e-beam evaporated palladium has also been shown to display increased solubility and decreased diffusivity.[530] In any case, from the divergent results described above, it is clear that this topic requires further study.

Film structure or texture is also an important variable.[211,212,354] For instance, texture as the result of cold working of the metal can affect hydrogen permeability.[546] Palladium without texture should have preferential orientation in the [111] direction. The adsorption enthalpy of hydrogen as well as surface diffusion on palladium depends somewhat on orientation.[212,411,547,548] During annealing or hydrogen absorption, the texture can change or recrystallization can occur (at temperatures as low as 300°C), affecting hydrogen permeability as well as membrane strength.[211,549–553]

Researchers often encounter an increase or decrease in the hydrogen permeation flux during palladium membrane operation at a specific temperature, chiefly during start up. Depending on the alloy composition, annealing at various temperatures can result in an increase or decrease in permeability and permselectivity due to structural changes induced by atomic ordering.[40,204,306,554–566] Annealing seems to densify films deposited onto porous supports by sputtering or electrodeposition.[348,409,567] Wu et al. noted an initial decrease in hydrogen flux that attained a steady state value after 80 hours and found that nitrogen flux decreased with increasing temperature (400–500°C).[568] They speculated that these phenomena were due to interactions between the palladium film and the titania support or rearrangement of the palladium film resulting in a decrease in the effective membrane area for hydrogen permeation.

The reason for increases and decreases in permeability at different temeratures remains unclear and may be ascribed to either atomic ordering, recrystallization, or segregation of impurities to the surface. Yeung et al. concluded that removal of impurities was not the reason for the increased permeability since the surface composition of a palladium film before and after annealing at 550°C was essentially the same.[560] Decline in hydrogen permeability during annealing at high temperatures (>600°C) has been noted by the authors.[569] Pd/alumina composite membranes have been observed to undergo a decrease in permeability with time online at temperatures greater than 550°C, apparently hastened by the tin impurity left behind during the standard surface activation process for electroless plating.[569] Residual gases trapped in the metal might also cause a flux decrease after running permeability experiments for an extended time with gases other than hydrogen.[375] This may be due to interference with hydrogen adsorption by the adsorbed impurity.[264,375,446]

## 1.2 The Alpha to Beta Phase Transition

Of great concern is the formation of two different palladium hydride phases ($\alpha$ and $\beta$ or $\alpha'$) that occurs with an increase in hydrogen concentration within palladium below the critical point of 293°C and $20.15 \times 10^5$ Pa.[258,365,570–575] Above 293°C only the $\alpha$ phase can exist while both phases may coexist below this temperature as hydrogen atoms increasingly occupy the octahedral interstices. Since the overall absorption limit of hydrogen in palladium is 67 atom % at one atmosphere and 20°C, the hydrogen atoms transition from occupying individual interstices in the $\alpha$ phase to partitioning inside the bulk metal into both the $\alpha$ and the $\beta$-Pd hydride phases.[576] This is accompanied by distortion of the metal and the production of dislocations due to the coexistence of two unequal face-centered cubic (fcc) phases with different unit cell sizes of 3.89 ($\alpha$) and up to 4.10 Å ($\beta$).[39,206,258,541,542,577–586] Nanocrystalline palladium may not fully experience the phase transition.[587]

Although the hydrogen permeability in the $\beta$ phase is higher than in the $\alpha$ phase and exhibits a maximum around 200°C, it is usually undesirable to operate in this state because of the internal stress as a result of the different lattice constants, principally when the membrane is cooled or the hydrogen concentration is changed.[588–592] Compounding this effect, consecutive hydrogen absorption/desorption cycles create defects causing the palladium structure to become disordered, thus, membranes fabricated from pure palladium may be destroyed by repeated exposure to hydrogen.[211,364] Known as hydrogen embrittlement, the manifestation of this phenomenon is warping and destruction of the membrane.[215,593,594] To avoid it, a pure palladium membrane must not be exposed to hydrogen at conditions where the β phase forms and should be thoroughly purged with inert gas prior to cooling from high temperature.

## 1.3 Palladium Alloys

Alloys of palladium possess properties that may help to allay some of the problems experienced by palladium membranes since the ability to withstand temperature cycling is virtually nonexistent with pure palladium films.[35,39] To begin with, the critical temperature and pressure for existence of the β-Pd hydride is lowered in palladium alloys (except with rhodium).[575] Alloys of palladium lower the critical temperature for the $\alpha \rightarrow \beta$ phase transition by narrowing the α/β-Pd hydride miscibility gap (pressure plateau in the phase boundary of the pressure-composition phase diagram) that pure palladium has below 293°C.[305,577,581,583,587,595–604] Furthermore, the difference between the sizes of the α- and β-Pd lattice constants is closer in alloys so less distortion occurs with successive hydrogen absorption-desorption cycles.[220,605]

Often alloying metals increase the permeability of palladium while substantially enhancing its mechanical properties.[606,607] Many palladium alloys are also more permeable to hydrogen than palladium itself including $PdAg_{25}$, $PdCu_{40}$, $PdRu_6$, and $PdY_{10}$ (compositions herein are in weight % unless otherwise noted).[45,212] For example, $PdAg_{25}$ absorbs hydrogen more quickly and is up to 1.5 times as permeable as pure palladium.[218] Alloys of palladium with silver result in two hydride phases that have lattice sizes closer than in pure palladium because the hydrogen solubility in the α and β phases is increased and decreased respectively.[602,608,609] For $PdAg_{23}$ and $PdPt_{19}$ (atom %) the critical temperature ($T_c$) for formation of the β phase is around room temperature.[203,305,610–616]

In addition, palladium alloys have higher tensile strength and hardness. This helps to eliminate membrane rupture, warping, or cracking, or failure associated with thermal cycling. Lattice expansion due to both hydrogen concentration and thermal dilatation is important when considering membrane durability during high temperature hydrogen separation.[40,266,550,558,617–622] Expansion must be accounted for in module design.[623,624] Alloys are sometimes more resistant to poisoning by contaminants such as sulfur and carbon. Specific alloy compositions can be created to perform a reaction.[60,166,487]

The Pd–Ag alloy has been studied extensively because of its higher permeability and increased strength compared to pure palladium. Pd–Ag membrane modules are employed commercially for special applications such as hydrogen isotope recovery, remote hydrogen generation or the ultra-purification of hydrogen.[625] Although considerably better than pure palladium, Pd–Ag has relatively low strength, still expands significantly upon hydrogen absorption, and experiences grain coarsening during extended periods at high temperature.[50,93,205,248,305,539,581,613,626] Beyond the increase in lattice parameter due to substitutional alloying, electronic effects such as donation of s and 3d-band electrons from silver to the 4d-band of palladium influence hydrogen permeability and adsorption of molecules onto the surface.[220,247,248,266,330,577,599,601,627–630]

Ternary and higher alloys of palladium have been developed to impart operating capability at high temperature and pressure. Addition of alloying elements with higher melting points than palladium can strengthen the membrane by suppressing grain growth, creep, and recrystallization.[631] Multi-component alloys with the transition elements, platinum group metals, or small additions of rare-earths raise the recrystallization temperature and help to maintain the plasticity and texture of the metal, especially at high temperatures.[40,203,549,608,613,621,631–642] Type V-series and B-series alloys have been developed containing four to six components, each composition tailored to a specific operation regime or reaction.[50,52,93,204,353,604,621,622,635,643–651] For instance, the V-2 alloy experiences very low dilatation upon hydrogen absorption allowing higher pressure differentials without stress rupture.[40,620,621] V-3 withstood 1000 cycles under hydrogen between 20 and 620°C before distorting.[646] $PdAg_{10}Ni_{5.5}$ has lower hydrogen permeability than the type-V alloys but experiences less hydrogen concentration dilatation.[550]

The addition of rare-earths such as yttrium and transition metals with larger atomic radii than palladium increases both the solubility and mobility of hydrogen partly because these elements expand the interstitial spacing.[229,242,266,305,577,630,639,652–668] These alloys are also harder.[266,305,577,669] While substitutional alloys may increase permeability, interstitial alloys often decrease hydrogen permeability by blocking hydrogen diffusion paths or acting as traps.[670,671] In the case of boron, this is presumably caused by distortion of these pathways by the atom in an interstitial position.[672]

From the literature, Pd–Cu alloys appear to have some superior properties. The advantages are lower cost (due to replacement of costly palladium with a much cheaper metal), enhanced thermal cycling properties (resistance to embrittlement), increased permeability, and sulfur tolerance.[451,673] The permeability passes through a maximum around 42% copper.[39,202,451,673–677] $PdCu_{40}$ has been reported to be up to 1.5 times as permeable as pure palladium at 350°C.[678] Like Pd–Ag, the copper alloy can withstand repeated temperature cycling with much less distortion than pure palladium, a primary issue in any system that endures periodic operation at temperature extremes.[678–681] Although the reason for the sulfur resistance of the palladium–copper alloy has yet to be explained, the increased hydrogen permeability supposedly depends on the formation of bcc structure by annealing below 600°C.[676,682–685] The increased permeability is attributed to an increase in diffusion coefficient and electronic effects may be responsible for this property.[686–688]

## 1.4 Methods of Palladium Composite Membrane Fabrication

Palladium composite membranes may consist of a variety of configurations. Solid tubes or foils may be rolled from the solid metal or from an alloy melt. Thin layers of metal may be deposited onto almost any substrate by physical or chemical vapor deposition. Electroplating can deposit palladium onto a metal substrate more economically than the above methods but for nonconductors such as ceramics another method such as electroless plating or solvated metal atom deposition is required. The basics of each are outlined below.

### 1.4.1 Rolling

Palladium alloys are prepared by melting and homogenization under inert gas or vacuum.[502] This is followed by cold working into the desired foil thickness.[12] Palladium alloy foils or tubes may be welded or brazed.[17,93,283,353,610,647] Tosti et al. report a method for rolling palladium-alloy foils (~50 μm) and welding them into the shape of a tube.[689,690] Annealing in between the cold rolling steps was necessary because of work hardening. Hydrogen can also be used to soften work-hardened alloys.[305] Maganyuk et al. used silver solder to form a 50 μm $PdRu_6$ foil into a cone for liquid phase hydrogenation of dehydrolinalool to linalool, a perfume component and pharmaceutical intermediate.[62,503,691] Adris et al. attached palladium and stainless steel tubes using a plasma needle beam welder.[692] Capillary tubes [1 mm diameter, <100 μm wall thickness) have been used with large pressure drops.[52,93,582,621,693]

### 1.4.2 Physical Vapor Deposition

Physical vapor deposition or PVD is the evaporation or ablation of a metal for condensation on the target surface.[694,695] A resistively heated piece of metal such as a wire can serve as the metal source. PVD can be advantageous for deposition onto polymers since the substrate can remain at room temperature.[91] PVD requires the use of costly vacuum chambers, clean conditions, and expensive metal alloy targets.[696] Another drawback is that the inside of a tube cannot easily be coated.[6] Nonetheless, PVD can be used to deposit very thin, continuous metal and metal alloy films. Several methods of PVD are described below.

In its simplest form, PVD involves vacuum evaporation of a metal by heating. Samples may be rotated to ensure even coverage. Adding a degree of complexity, sputtering with an electron beam (e-beam), laser, ion gun, or plasma can remove material from the target to be deposited on the substrate.[696,697] Although coating thickness is easily controlled using PVD, because the metal flux impinges at a certain angle, substrate rotation must occur during deposition to avoid shadowing, or uneven coverage of the surface leading to voids and porosity.[96,698,699]

Incident flux, presence of contaminants, substrate temperature, substrate material, crystallinity, and orientation determine the microstructural evolution of the thin film and must be considered to deposit a metal film with the desired characteristics.[327,567,698,700–702] Differing sputtering yields often complicate the deposition of alloys. For example, Athayde et al. tried to deposit $Pd-Ag_{23}$ (atom %) but the film was palladium-rich relative to the sputtering target. This problem can be overcome by shielding the substrate and sputtering long enough to reach target equilibration before depositing on the substrate.[703]

### 1.4.3 Magnetron Sputtering

Magnetron sputtering takes place when a plasma (glow discharge) induced by a gas (typically Ar) introduced into the vacuum chamber dislodges atoms and ions from the metal target to be deposited on the desired surface.[695,704,705] The fields of permanent magnets increase ionization. Ample ionization, high current density, and high sputtering rates are required to deposit a dense, continuous film. The same problem of alloy target equilibration applies to magnetron sputtering.

### 1.4.4 Ion Plating

To deposit a chemical compound or influence the properties of the deposit, ions of inert or reactive gas bombard the metal evaporated or sputtered from the target during PVD. Either an ion gun or plasma can provide the ions.[696]

### 1.4.5 Chemical Vapor Deposition

Referred to as CVD or metal-organic chemical vapor deposition (MOCVD), this method takes advantage of a compound with a sublimation temperature below its decomposition temperature.[694] During composite metal membrane fabrication, the organometallic material is usually sublimed in a separate chamber, transported using a carrier gas, and thermally decomposed at the desired surface or reacted with a gas such as hydrogen. The precursor may also be decomposed in a plasma.[706] Common CVD precursors are palladium(II): acetate; acetylacetonate (acac); bis(hexafluoroacetylacetonate) or $(hfac)_2$; and chloride.[38,117,707]

A major advantage of CVD is that metal can be more easily deposited within the support pores as opposed to only on the surface as is the case with electroless plating and PVD.[708,709] This enables much thinner palladium films to effectively block the pores of a porous support. The disadvantages of CVD include contamination of the film with constituents of the organometallic complex such as carbon. Another problem that CVD shares with PVD is buildup of expensive precious metals on non-target surfaces.[710] The organometallic precursors can also be exorbitant in cost, or if not commercially available, difficult to synthesize.[711]

### 1.4.6 Spray Pyrolysis

Spray pyrolysis involves the entrainment of a metal powder in a high temperature flame. The metal is carried to the substrate at high velocity in a semi-melted state.[436]

### 1.4.7 Electrodeposition

During electrodeposition, a power source supplies the electrons for reduction of metal ions onto the substrate from solution. For pulsed electrodeposition, the current is modulated in order to produce alternating metal deposition/removal cycles. In this manner, film parameters such as grainsize, stress, and composition can be well controlled.[509,712–714]

### 1.4.8 Electroless Plating

Also known as electrodeless, chemical plating, liquid phase epitaxy, or autocatalytic plating, electroless plating is the deposition of metals using chemicals as the source of both metal and electrons. Electroless plating is autocatalytic in that the deposited metal catalyzes further deposition.[715–719] A full understanding of its nuances is a key to the production of thin, adherent, pore-free metal films on various substrates. Electroless plating techniques have been developed for many elements including palladium.

Electroless plating is commonly used to deposit palladium films because of its throwing power (coverage of surfaces), ease of implementation, and the ability to deposit on nonconductors.[720] There are many challenges in depositing thin but impervious (impermeable to gases other than hydrogen) palladium films. First, if the surface is nonconducting or noncatalytic for electroless deposition, it must be well activated to promote even coverage and good adhesion of the deposit. Also, the support should be relatively smooth and free of macrodefects. The focus of the following discussion is the sensitizing/activation process, the plating bath operatives, and the interplay among the many parameters required for making a thin, stable and selective membrane by electroless plating.

Electroless plating occurs through an autocatalytic reaction mechanism that is initiated by an activated surface.[715,721,722] The substrate is activated prior to the plating operation by seeding the surface with metal crystallites (usually gold, silver, platinum or palladium). This is required to initiate plating and ensure adherence of the film. The metal nucleation sites initiate the electroless plating reaction by catalyzing the decomposition (oxidation) of a reducing agent in the plating bath.[723] Electroless plating is performed by immersion in a plating bath containing the appropriate constituents at the optimum temperature and concentrations to produce the desired microstructure and plating rate.

Electroless plating has several advantages compared to other deposition methods. It has excellent throwing power (coverage of surfaces), in contrast to electroplating where deposition is sensitive to the current density (electric field) on the substrate.[724,725] Electroless plating can also coat nonconductors with proper surface activation. It requires no expensive electronic equipment, vacuum chambers, metal targets, or organometallic precursors. Some major drawbacks of electroless plating are that it uses highly toxic chemicals and generates hazardous liquid wastes.

### *1.4.8.1 Surface Cleaning*

Prior to any deposition process, the porous support must be cleaned. Contaminants must be removed to ensure that an adherent, uniform, and defect free deposit can be obtained. Cleaning may be accomplished with a variety of solvents and cleaning agents without altering the membrane characteristics. Typically, surfaces to be plated are washed in mild detergent, dilute acid or base, followed by rinsing in alcohol or acetone and deionized water. Hydrogen peroxide is another effective cleaning agent.

Adhesion to ceramic substrates may also be enhanced by certain chemical treatments before plating. For example, etching of alumina has been shown to increase adhesion.[273,726–728] Soaking in $NH_4F$, HF, or NaOH cleans and roughens the surface, possibly removing some glassy phase impurities from alumina such as amorphous silicates.[729,730] During high temperature processing of alumina membranes, lower melting glassy phases such as $SiO_2$ and impurities may segregate to the surface between the alumina grains. Dissolution of some of this glassy phase on the surface helps to anchor the palladium film by creating a network of pores or pits. Metal/ceramic adhesion of films deposited by electroless plating depends primarily on mechanical bonding.[731] Ameen et al. observed that on 96 and 99.5% $\alpha$-alumina, etching away the vitreous binder components of the alumina with ammonium or sodium fluoride resulted in high pull strengths but destroyed some of the ceramic.[726]

While the above cleaning techniques work well for ceramic substrates, metals such as stainless steel require different preplating preparation conditions.[6,99,332,732–736] Metals have an omnipresent oxide layer that must be removed. This is accomplished via mechanical cleaning or acid pickling steps. To prepare a porous stainless steel membrane for electroless plating, it was placed in concentrated hydrochloric acid for 5 min., rinsed, and treated in $\sim$40% phosphoric acid.[737] Plating must immediately follow the cleaning step (after rinsing) to prevent the oxide layer from reforming. Metals are often activated with what is called a strike where an acidic metal bath removes the oxide layer and electrodeposits a layer of metal active for further metal deposition.[738,739] Once cleaned and activated, metals can be plated using electroless or electroplating procedures.

To convert stainless steel from a hydrophobic to hydrophilic surface, chromic and sulfuric acids with surfactants have been used.[740] For example, stainless steel was dipped in 25–50% $H_2SO_4$ at 70–80°C for 30–75 seconds prior to electroless plating.[733] This acid pickle (as it is called in the trade) or chemical activation removes contaminants in addition to stripping the oxide layer to expose more active metal for subsequent deposition.[716] A more stable oxide layer can form if the conditions of this pretreatment are too severe. Many highly effective preparations are commercially available.

### *1.4.8.2 Surface Activation*

After cleaning and before electroless plating, it is necessary to activate the surface of a non-conducting substrate. Traditionally, this is accomplished with tin chloride sensitizing and palladium activation baths.[741–743] This forms the metal nanoclusters on the surface requisite for initiation of electroless plating.[744] Surface activation is mostly for catalyzing the electroless plating reaction while adhesion of the resulting deposit is primarily by mechanical keying with the support.[745,746] The chemistries of the sensitizing and activating processes have been thoroughly studied.[747–778] An overview of the procedure follows.

There are two types of activation processes using tin and palladium chloride, either sequential or mixed. In the sequential method, substrates are immersed in separate tin chloride and palladium solutions with rinsing in between. Mixed activators consist of a combination of tin and palladium salts in one bath. It has been noted that the two-step procedure has more attributes desired for palladium membrane fabrication: higher surface coverage and less tin deposition.[779] The sequential sensitizing-activation procedure begins with immersion in an acidic $SnCl_2/SnCl_4$ colloidal sensitizing solution followed by acidic palladium containing activating solution. The colloidal tin solution is required to anchor the palladium to the surface.[746] Upon immersion in palladium activating solution, tin binds palladium to the surface via the reaction,

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^{0},$$

creating a Pd–Sn alloy on the substrate.

The tin should resolubilize in the acidic palladium activation solution, but in practice much remains on the surface. Tin-rich surface layers usually cover the active palladium cores.[767] Although activity has been found to depend on the Sn/Pd ratio, excess tin accumulating on top of the palladium crystallites blocks their activity in catalyzing hydrazine oxidation.[723] Rinsing after activation is required to prevent ‘‘drag-in’’ of the sensitizing and activation bath components into the plating bath.[716–719,780] Otherwise, spontaneous decomposition of the bath may occur as the catalyst creates many nucleation sites throughout the plating solution.

Charbonnier et al. provided a good overview of tin and palladium activation processes and mechanisms as well as a review of relevant literature.[749,750] These reports concluded that tin chemisorbs preferentially onto substrate oxygen followed by palladium attachment via chlorine ions adsorbed on tin. Although their work involved polymers, the mechanism can probably be extended to alumina with its surface hydroxyl groups. When the colloidal tin particles contact the substrate, $Sn^{2+}$ adheres to the surface, probably by a mechanism shown in Figure 1 (adapted from Charbonnier et al.,[750] Hulteen et al.,[781,782] and Menon and Martin[783]).

Silvain et al. reported the formation of Sn–O–Pd bonds on the surface of NiTi(O) observed with X-ray photoelectron spectroscopy (XPS) and depth

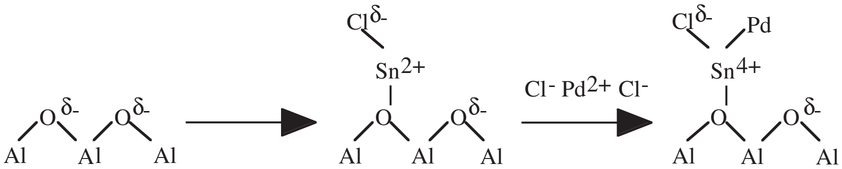

***Figure 1.*** Possible mode for sensitizing/activation of alumina surface.

profiling after activation with the two-step activation procedure. After submersion in the tin solution the surface was almost completely covered with an approximately 3 nm thick layer of tin and tin oxides (SnO and $SnO_2$). The tin had actually replaced nickel in the $Ni_2O_3$ forming $SnO_2$ and nickel. The palladium activation step resulted in 2 and 3-dimensional nanometer sized palladium islands and palladium oxide enveloped by a tin and tin oxide layer along with small amounts of chlorine compounds ($<1\%$). When copper was deposited by electroless deposition it interdiffused into the activated layer resulting in strong adhesion.

Several studies have been performed on the stability of tin sensitizers.[784,785] Tin sensitizers are photosensitive, so exposure to ultraviolet light should be avoided to prevent photo-oxidation.[784] Oxidation of the colloidal tin sensitizing solution is detrimental to its efficacy and can be prevented by storing the solution under an inert gas blanket or by bubbling Ar through the solution.[731,784]

Palladium *electrodeposited* onto stainless steel substrates and then air dried has resulted in the formation of divalent palladium oxide (PdO) whereas tetravalent palladium(IV) oxide ($PdO_2$) formed on air dried *activated* substrates.[715] In the latter case, uniform activation particles of $\sim 500$ Å diameter were easily oxidized to both palladium(II) and palladium(IV). Oxides interfere with the catalytic properties of the activation layer. Palladium oxides of higher valence ($+4$) appeared to be electroinactive towards hydrazine oxidation although hydrazine reduced palladium(II) oxide to palladium(0) upon immersion in electroless plating solution.[715] Even oxygen dissolved in the sensitizing or activating solutions can passivate the catalytic sites on the substrate.[731]

Excess tin can be removed from the activated surface by performing a technique called acceleration. This entails briefly soaking the membrane in a solution of acid, base, or complexant to dissolve away excess tin and tin oxides after performing the sensitizing-activation procedure.[745,760] Water, with a pH of 7, is a poor solvent for tin removal although rinsing in water is not detrimental to coverage of the surface by Pd/Sn catalyst. Disodium-ethylene-diamine-tetraacetic acid ($Na_2EDTA$) is effective at acceleration with the advantage of being non-toxic and usable over a large pH range. Without acceleration, the tin coverage can be greater than that of palladium.[762] Tin shields the palladium crystallites from the plating bath reactants, reducing their catalytic activity by inhibiting the hydrogen sorption capability.[723] By removing the tin compounds that mask the catalytic activity of the palladium nuclei, the induction time before electroless plating commences is shortened.[769] Palladium coverage has been found to remain constant during acceleration although it can cause rearrangement of the Pd/Sn islands on the activated surface.[762] The state of the palladium crystallites after acceleration depends on the accelerating agent.[768,769] Membranes have previously been fabricated using acceleration in the sensitizing-activation process prior to electroless plating.[188]

Before acceleration, drying of the substrate must also be prevented since the active particles react with oxygen forming difficult to remove compounds that prevent initiation of metal deposition.[786] None of the accelerators dissolve highly insoluble $SnO_2$ from a dried surface.[762] After washing and drying the substrate, tin not in the Pd–Sn core is in the hydrated Sn(IV) oxide state. Acceleration removes tin by a factor of 3 to 10 resulting in a Pd/Sn ratio of $\sim 3$. Tin remaining after activation may dissolve into the electroless bath to be codeposited with the plating metal.[765,766]

The structure of the palladium clusters on the substrate that initiate electroless plating may also influence the structural characteristics of the deposit that are dependent on the nucleation and growth process.[787] The coverage, adhesion, and porosity of the film are a function of catalyst activity and dispersion.[723] The primary activator deposit strongly affects film growth while bonding between the film and substrate occurs through metal–oxygen bond formation at the interface.[788] The morphology of the substrate can be expected to have a strong influence on the structure of the deposit as well.[787,789] Adhesion also depends on the amount of tin and palladium adsorbed on the substrate during sensitizing/activation.[745] Furthermore, the higher the surface coverage by the activating metal, the better the coverage by the depositing metal and the less porous the deposit will be.[739,746] Number and size of the metal grains on the substrate affect the catalyst activity.

A disadvantage of the Pd/Sn activation process is that contamination of the subsequently deposited palladium film with tin from the sensitizing bath has been shown to lower the temperature where pores form in the palladium and adversely impact the high temperature membrane stability.[569] An alternative for catalyzing alumina surfaces for electroless plating is to use methods ordinarily used for catalyst preparation. Nanoscale metal clusters on the substrate created by impregnation, incipient wetness, or ion-exchange could serve as sites for initiation of electroless plating or actually create the permselective layer.[790,791] This notion was experimented with by Li et al. who deposited a $\gamma$-alumina sol-gel layer containing $PdCl_2$ onto an $\alpha$-alumina support to reduce the pore size and catalyze the electroless plating reaction.[792]

Other methods for surface activation also eliminate tin by depositing an organometallic precursor from solution followed by treatment with heat, laser, plasma, or ultraviolet light to remove the organic fractions.[793–796] Sodium borohydride ($NaBH_4$) can also be used to reduce the organometallic to pure metal. In theory, any technique may be used to deposit a metal seed layer to promote electroless deposition, as long as the metal catalyzes decomposition of the reducing agent.[797,798] Wu et al. activated a porous titania membrane by using a photocatalytic reaction and $PdCl_2$.[568,799] The palladium film deposited by electroless plating onto the well-dispersed palladium activating layer was thin (0.3–0.4 μm), adherent, and had a high $H_2/N_2$ permselectivity (1140 at 500°C). Schwartz et al. developed an activation technique for ceramic supports that involved the deposition of palladium acetate from solution, followed by heat treatment to burn off the organic fraction and leave behind palladium particles.[117] An advantage of this procedure is the elimination of wastewater generated from the sensitizing and activation procedure.[273]

### *1.4.8.3 Microstructural Evolution During Electroless Plating*

Since the plating rate and film morphology depend on many variables such as concentration of bath constituents and plating temperature, understanding the fundamentals of electroless plating is the key to optimizing the conditions for producing usable palladium and palladium alloy films on various supports. Palladium film structure in composite membranes has been linked to limitations in high temperature stability, resistance to thermal cycling, and minimization of the defect-free film thickness.

Therefore, control of electroless plating methods is critical. Grainsize and film porosity can vary widely depending on electroless plating bath concentration, composition and plating temperature.[800] Preferably the coefficient of thermal expansion of the support matches that of palladium to reduce stress build up in the deposit.[801,802] Deposition under an osmotic pressure gradient (‘‘osmotic plating’’) by conducting electroless plating with a more concentrated solution on the opposite side of the porous support has been shown to produce thinner palladium films that are more impenetrable to permeation of gases other than hydrogen.[198,803–807] Zheng and Wu deposited palladium in a closed system so that the pressure increased during plating.[808,809] This appeared to promote better pore closure by the depositing metal. To obtain uniform deposition during electroless plating the solution should be mildly agitated (or the solution flow reversed) to remove bubbles that form and obstruct deposition, creating pores.[810] Substrates should be inverted periodically if plated vertically or rotated if plated horizontally.[304,436]

During electroless plating, electrons are released by the anodic partial reaction and consumed by the cathodic partial reaction:[811,812]

$$R^0 \rightarrow R^{z+} + ze^-$$

$$M^{z+} + ze^- \ \rightarrow \ M^0$$

Here, $R$ is the reducing agent, $M$ is the metal and $z$ is the number of electrons transferred. For deposition to occur the sum of the standard redox potentials ($E^\circ$) of the oxidation and reduction reactions must be positive and $\Delta G^\circ$ (Gibb's free energy) be negative so that the reaction is thermodynamically favorable.[724] However, if the sum of the redox potentials is too high, the bath will be unstable and spontaneously decompose.

Electroless palladium plating baths normally consist of a palladium–amine complex stabilized by a chelating or sequestering agent such as $Na_2$EDTA. Plating bath stability dictates the amount of reducing agent that can be added. According to early work by Rhoda on the subject, the primary factors influencing electroless plating of palladium are the metal-ion concentration, temperature, and hydrazine concentration while amine solvent and stabilizer (EDTA) concentrations are secondary.[741–743] Bath pH is usually around 11 depending on the ammonium hydroxide ($NH_4OH$) content. Controlled deposition of palladium from the stabilized bath is accomplished by the introduction of a suitable reducing agent:[720,743]

$$2Pd(NH_3)_4^{++} + N_2H_4 + 4OH^- \ \rightarrow \ 2Pd^0 + 8NH_3 + N_2 + 4H_2O.$$

Vigorous agitation of the plating solution can occur due to gas production. Gases adhering to or trapped in the film during deposition can result in a discontinuous deposit or ''skip'' plating. The reaction may also be broken up into anodic and cathodic half-reactions:[734]

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-;$$

$$2Pd^{2+} + 4e^- \rightarrow 2Pd^0.$$

Beginning film structure is largely dependent on composition and concentration of palladium in the plating bath with plating conditions strongly influencing subsequent porosity. Electroless films form by a sequence of distinct steps.[179,188,560] Microstructural evolution transpires with nucleation and ensuing 3-dimensional growth from catalytic centers on the surface.[188,785] First, nucleation takes place when the palladium on the activated surface catalyzes deposition. These tiny particles grow and the crystals coalesce into larger particles, eventually forming a continuous film. The final grain structure depends on this initial nucleation and growth process as well as the structure of the substrate.[725,785] Generally, large (submicron to micron sized) crystallites form that are comprised of much smaller grains ($<100$ nm).[808]

In addition to the catalytic activity of the substrate, metal-ion concentration in the electroless plating solution highly influences film microstructure by affecting the nucleation rate. Supersaturation, brought about by higher concentration, increases the nucleation rate resulting in the formation of copious tiny palladium particles. These small particles posses high chemical potential and pack tightly into a dense film to minimize surface energy. With dilute plating baths, crystal growth is faceted due to lack of supersaturation. In that case, a low rate of mass transfer to the surface leads to nucleation inhibited growth where diffusion of metal complex to the substrate controls deposition. Therefore, at lower metal-ion concentrations, adhesion is improved because the nuclei are well distributed on the substrate in the initial stages of plating.[715,731] Indeed, pull strength increases with decreasing metal-ion concentration in the bath.[739] While such well crystallized films adhere better to the substrate, they contain pores due to loose packing making them unsuitable as membranes.[800]

Shu et al. ascertained that the brighter film from a concentrated bath consisted of tightly coalescent surface grains with no favored crystal orientation in contrast to the tapered, loosely packed crystallite particles obtained from a dilute bath.[800] The dilute bath with low metal content resulted in large grains separated by voids, suggesting that the concentrated bath is more desirable for creation of a coherent film. However, the film deposited from the dilute bath adhered more strongly to a stainless steel support.[800]

Electroless plating is either diffusion or electrochemically (activation) controlled. Depending on the conditions, diffusion of reactants to the surface, or the reaction on the surface can be rate determining.[813] In diffusion control, mass transport or diffusion of $[\mathrm{PdEDTA}]^{2-}$ complex to the surface followed by reduction (after dissociation of the metal complex) controls the rate.[814] This results in some interdependence of the two partial reactions.[811] For instance, electroless copper plating rate has been found to be heavily dependent on agitation at low copper concentrations while during operation in kinetically (electron transfer from the reducer) controlled regimes the rate was zero order with respect to copper ion concentration. The reaction is likely to be diffusion limited on rough surfaces due to the thicker diffusion layer.[724]

Anodic oxidation of reductant is usually under activation process control and not affected by agitation of solution while the partial cathodic deposition process is frequently controlled by diffusion (metal complex transport to the surface).[744,814] The two partial reactions are interdependent when they proceed simultaneously.[814,815] The electroless palladium reaction is said to be under mixed potential control; diffusional (palladium complex) and electrochemical (hydrazine decomposition kinetics).[814,816] The slower of the two reactions determines the rate of metal deposition.

Several studies have looked at electroless plating rates in relation to palladium composite membrane fabrication.[304,779] Collection and analysis of the gases produced is an accurate way to measure palladium deposition rate.[779] Shu et al. established that hydrazine oxidation is the rate-limiting step in electroless palladium deposition onto stainless steel, i.e. hydrazine adsorption and dehydrogenation controls the rate of palladium deposition.[715] Yeung et al. have studied the plating kinetics of a hydrazine based electroless palladium plating bath and found that hydrazine is the limiting reactant.[560,817] A quartz crystal microbalance was used to monitor the amount of metal being deposited.[818] Zhao et al. found that higher concentrations of hydrazine in the plating bath produced more compact and permselective palladium films.[819] The increased deposition rate from higher reducer concentration resulted in smaller metal particles. In the presence of catalyst (palladium), hydrazine also decomposes:[779]

$$2N_2H_4 \rightarrow N_2 + 2H_2.$$

A high hydrazine/metal ratio in the bath can also increase the plating efficiency (fraction of palladium deposited from the plating bath).[779,818] To obtain better plating efficiency and a more constant plating rate, hydrazine should be added incrementally to account for its decomposition and prevent the bath from precipitating by adding too much at once.[198,560,779]

The oxidation kinetics of the reducing agent greatly influence electroless plating bath performance. Hypophosphite based baths possessing greater stability and plating efficiency have been used to prepare palladium composite membranes.[806,812,815,820] However, hydrazine is a superior reducing agent for palladium membrane fabrication since hypophosphite tends to deposit 3–14 atom % P that is incorporated into the palladium film, leading to brittleness and probably a reduction in hydrogen permeability.[6,99,817,821,822]

Addition of ammonium hydroxide to the plating solution raises the pH and supplies the hydroxyl ions that are consumed by hydrazine oxidation. It also stabilizes the bath by complexing with palladium although too much will inhibit deposition. As the alkalinity of the bath increases, metal ions can hydrolyze to metal hydroxides that precipitate out.[823] Excess ammonium hinders this tendency. Bath decomposition is deleterious as it necessitates replacement of the electroless plating solution and plating container. Also known as palladium black because of its appearance, palladium nanoparticles are sometimes desired on the surface of the palladium membrane since it increases membrane permeability as well as catalytic activity by increasing the metal surface area.[258,288,380,497,589,598,824–828]

Plating temperature also has a significant impact on film morphology. The lower the temperature, the larger the crystallites that are formed while faster plating at higher temperatures creates palladium films that are amorphous with smaller, more closely packed crystallites resulting in a denser structure with smaller grainsize as well.[812,815,820,829,830] Supposedly, the latter is more desirable for producing a thin, defect-free film with greater hydrogen permselectivity. Better quality deposits have been obtained at higher plating temperatures because compressive stress and lattice strain are reduced.[831] Expedited nucleation at higher temperatures allows the depositing atoms to consolidate into the crystal lattice without strain. Moreover, if plating rate is too rapid, nanoscale voids may form in the coating where swiftly spreading deposition growth fronts coalesce.[731] Hydrogen absorbed by the deposit during the plating process can cause hydrogen embrittlement of the film that results in blistering.[787,817]

Concentration of the ligand complexing agent in the electroless palladium solution is of considerable importance with respect to deposition rate and film morphology.[779] The chloride anion of the palladium salt is not completely removed from the coordination sphere of the metal ion but is in equilibrium competition with the organic complexing agent EDTA and solvent molecules (water and hydroxyls) for the coordination positions of the metal ions.[720] The complexed palladium diffuses to the solid–liquid interface and deposits by capturing electrons from the catalytic surface (supplied by oxidation of the reducer) and returning to the zero valence metallic state.[812] Free metal ions are the product of ligand complex dissociation:

$$(Pd_mL_n)^{2m-nz} \rightarrow mPd^{2+} + nL^{z-},$$

where $L$ is the ligand, $m$ and $n$ are the metal and ligand coordination numbers respectively, and $z$ is the charge on the ligand.[812]

Stability of the electroless plating bath is imparted from a shift in the reduction potential due to the increased number of coordination positions of the plating-metal ion filled by ions of the ligands with which it is compounded.[832] As a strong complexing agent for palladium ions, high concentrations of EDTA slow down the metal complex dissociation reaction by decreasing the availability of metal ions to be reduced.[734] Then the dissociation reaction to free palladium ions from the stable EDTA complex becomes the rate-determining step in electroless plating, corresponding to a slow deposition rate.[820] Adding a high concentration of stabilizer is the same as lowering the effective concentration of metal in solution, promoting the growth of large crystallites.[800] Since cathodic overpotential is directly proportional to metal complex concentration, smaller grains and continuous films form at higher complex concentration due to the slow release of metal cations from metal complex dissociation.[812]

Other additions to the plating bath affect plating rate and film structure. The effect of formaldehyde (HCHO) addition to electroless plating baths has been studied by Yeung et al. and the mechanism for its decomposition to formate ion has been studied by Bindra et al. and Horkans et al.[761,762,816,833] Formaldehyde oxidation is under kinetic control where the first step is dissociative adsorption into a carbon containing fragment and $H^+$.[762] Formaldehyde acts as a moderator and produces smaller, more uniform grains. In excess it inhibits plating completely and its presence is not conducive to high palladium conversions in the electroless plating bath.[779,805,806]

### *1.4.8.4 Formation of Palladium Alloys*

Although several researchers have performed electroless codeposition of palladium and silver, controlling the film composition is tricky.[179,734,805,818,834–836] Another option is to deposit the metals separately and then anneal.[837–841] To obtain an alloy film from two distinct metal layers in a reasonable amount of time, a high enough temperature must be utilized to promote complete metallic interdiffusion. Pd–Ag alloy films have been fabricated by several research groups using such sequential deposition and annealing.[179,185] Shu et al. annealed a *codeposited* Pd–Ag film for 150 minutes at 400°C and a *sequentially* deposited Pd–Ag film for 5 hours at 550°C.[734] Cheng and Yeung studied the kinetics of Pd–Ag codeposition from a mixed electroless plating bath and were able to control the alloy composition.[818] Annealing for 8 h at 500°C formed a uniform alloy. Hydrogen accelerates the alloying process by facilitating metal atom diffusion.[842–846]

Interestingly, when Keuler et al. deposited several microns of palladium and silver, depositing palladium first resulted in much better adhesion to the support.[847] The membranes were heated for 5 h at 650°C under hydrogen. On the other hand, the film was more homogeneous after heat treatment when silver was deposited first. In contrast to silver, nickel deposited onto palladium resulted in the formation of a metal layer with completely homogeneous composition during the same heat treatment schedule.[848]

## 1.5 Membrane Supports

Minimizing the palladium loading has been the driving force behind development of composite membrane configurations. A variety of deposition processes and supports have been used. The simplest technique involves compressing or diffusion welding a palladium alloy foil onto a refractory metal foil or a macroporous support such as compacted stainless steel particles.[30,44,193,329,377,849–852] The types of supports commonly used in palladium composite membrane fabrication are outlined below.

### 1.5.1 Porous Supports

Palladium films are frequently supported by a porous membrane. Membranes made of ceramic, Vycor glass, or stainless steel are commercially available.[853] Each type of support has economical and performance tradeoffs. Some merits of stainless steel are sturdiness and weldability.[737] Alumina is resistant to chemical attack and is stable at high temperatures.

Pd/ceramic membranes are the most prevalent type of composite due to high permeability, and the ability to withstand high temperatures. Both symmetric and asymmetric ceramic supports are used.[35] The tubular geometry is popular but disks are often used as well. Asymmetric membranes are distinguished by a relatively thin selective layer of smaller particles coated on the surface of the bulk of the membrane comprised of larger particles. Titania, $\gamma$-alumina, and silica are popular top layers and angstrom pore sizes are attainable. Asymmetric supports have much less resistance to flow since the fairly dense selective layer is very thin relative to the much more porous wall of the tube.

Asymmetric membranes are manufactured by coating the inner diameter of an extruded and fired highly porous support with successive dip-coatings, slip-castings, or sol-gel layers of progressively smaller particles.[116] Curing and firing may be required between each deposition and special treatment processes are required to prevent cracking of the asymmetric layer. Whereas asymmetric membranes function well as supports for palladium membranes due to their smooth surface and low resistance to gas flow, the high cost of the multistep manufacturing process makes them relatively expensive compared to other porous supports. Symmetric membranes have the same pore size throughout the wall and are produced in one extrusion or casting and firing sequence so that lower cost is their primary advantage. The major negative of a symmetric support is its higher resistance to flow.

Asymmetric membranes sinter at lower temperatures because of the layer of very high surface area material. For example, the pore size of 40 Å $\gamma$-alumina membranes will increase at 550°C.[854] Titania undergoes a phase transformation as low as 300°C[855,856] while zirconia ($ZrO_2$) and $\gamma$-alumina are stable up to $\sim$600°C.[117,192] Zirconia can be stabilized with yttria ($Y_2O_3$).[415,779,857,858]

Porous metal supports are fabricated by compressing or sintering together very fine metal particles. Porous metal membranes are sturdier and easier to seal (by welding or brazing) in an industrial setting than more fragile ceramic supports and their cost falls between symmetric and asymmetric ceramics. Of course, with the economy of scale, the price of each type of membrane would be expected to drop significantly. Porous metal supports are also frequently used to form palladium composite membranes. Stainless steel is primarily used although porous silver discs have also been adopted as a palladium membrane support.[822] Jarosch et al. used porous Inconel (0.2 μm pore size) as a support.[859] An advantage of porous metal is that its coefficient of thermal expansion is closer to that of palladium than ceramic supports, resulting in less stress during thermal cycling.[801,802] The smallest pore size commercially available in a porous metal tube or disk is 0.2 μm. The surface roughness or non-uniform pore distribution of porous metal supports is the limiting factor in obtaining a thin, non-porous palladium film on the surface.[117]

Two other types of commonly used supports are porous borosilicate (or Vycor) glass and anodic alumina. Vycor is available in uniform symmetric pore sizes as small as 40 Å.[860] It was one of the first supports to be used to fabricate selective palladium composite membranes.[180,861,862] However, porous glass can sinter above 550°C causing pore structure collapse and can also undergo hydrothermal sintering (>450°C).[179,192,854,860,863,864] Very small (nanoscale), uniform, and straight pores can result from anodizing aluminum into alumina except it is less frequently used as a palladium membrane support due to its fragility and limited temperature range of stability.[737,865,866] Porous anodic alumina membrane supports can be formed by electrochemical oxidation of an aluminum foil or tube in oxalic acid.[58,867,868] Thin (1–2 μm) palladium alloy films have been deposited onto anodic alumina foils that were sealed into an apparatus along the nonporous edges of the aluminum foil.[58]

By first sputtering and then electroplating, Itoh et al. deposited palladium films that were several microns thick inside anodic alumina tubes that had pores on the order of tens of nanometers.[867] The hydrogen/nitrogen ideal separation factor was 1640 at 350°C when a current density of 100–200 A/$m^2$ was employed for 24 min. of electroplating to plug the pores with a 4 μm thick film. Their report also provides a comparison of palladium composite membranes fabricated by a variety of methods. Comparison of the membranes made by many different researchers to decide on the best method of metal film deposition is difficult due to performance variability that is a consequence of the incomplete stage of technological development for each composite membrane type.[867]

### 1.5.2 Influence of Support on Palladium Composite Membrane Fabrication

Surface chemistry, porosity, and roughness of the support will determine the amount of palladium required to form a hydrogen permselective film without pores. Greater surface roughness and larger pore size will necessitate a thicker layer of palladium in order to span all of the pores and cover the surface of a supporting membrane.[46,276,567,869] Furthermore, microscopic debris may create defects in a palladium film.[409] For example, it has been indicated that the use of clean-room conditions during the fabrication of silica membranes drastically decreased the number and size of defects in the permselective layer.[65,870] Each type of substrate (and deposition method) has its own characteristics that determine the amount of palladium that will be needed. As an illustration of the effect of pore size on composite membrane preparation, Yildirim et al. determined that at least 4 μm of palladium deposited by magnetron sputtering onto Vycor glass with 4 nm pores was necessary for a leak-free film.[871] Backing up this assertion, Gobina et al. obtained 6 μm thick pinhole-free $PdAg_{23}$ films deposited by magnetron sputtering onto Vycor.[872–874] A dense film was not attainable by sputtering onto a support with 12 μm pores.

Zhao et al. correlated the gas tightness of a Pd–Ag film with the surface roughness of the γ-alumina sol-gel layer it was deposited on.[869] Quicker et al. reported that CVD of palladium onto alumina with 0.1 μm pores was unsuccessful although better results were realized using supports with 4 nm pore size while Jayaraman et al. concluded that the number of defects in Pd–Ag films sputtered onto γ-alumina depended on the pore size and surface roughness of the support.[436,567] Deng and Wu used electroless plating to deposit ~20 μm palladium onto the outer diameter of porous ceramic with 0.5 μm pore size.[875] Nitrogen could not be detected on the permeate side of the membrane during permeation experiments. On a porous γ-alumina support, Gryaznov et al. deposited a defect-free composite film consisting of a 0.17 μm layer of $PdRu_6$ on top of 0.04 μm of tantalum.[691]

It appears that porous metal supports may require a relatively thick layer of palladium compared to similar porous ceramic supports to form a pore-free film. This may be due to inherent manufacturing imperfections in the form of large pores or high surface roughness. Nam et al. discovered that because of the roughness of 0.5 μm porous stainless steel supports, macropores remained unplugged even after depositing 10 μm of Pd–Ni. Gryaznov et al. were able to obtain a leak-free composite membrane with 10 μm of Pd–Ru on similar supports.[62,348,876] Shu et al. found that stainless steel supports with nominal 0.2 μm pores required at least 15 μm of metal deposited by electroless plating to form a dense, impervious film.[801,877] More recently, Mardilovich et al. and Lin and Rei reported palladium film thicknesses between 19–28 μm electroless plated onto porous stainless steel supports that had a nominal 0.5 μm pore size.[304,878] Quicker et al. discovered macrodefects (>50 μm) that spoiled an otherwise continuous coating on a porous stainless steel tube.[436] Finally, Jarosch and de Lasa consumed 70–100 μm of palladium to coat 0.2 μm porous Inconel.[859]

Exceptions to the above results have been obtained on porous stainless steel by using osmotic plating (described above) or vacuum electroplating. Yeung et al. obtained a membrane with a hydrogen/nitrogen permselectivity of ~100,000 using osmotic plating.[198] This membrane withstood repeated thermal cycling between 350 and 600°C without loss of permselectivity while membranes prepared using ordinary electroless plating did not. Without osmotic pressure, Cheng and Yeung used ~18 μm of palladium to form a dense membrane on porous stainless steel.[817] Li et al. deposited a 10 μm thick palladium film onto porous stainless steel using osmotic plating and the resulting membrane had a hydrogen/nitrogen permselectivity of over 1000.[879,880]

The average pore size of porous metal supports can be reduced by mechanically altering the surface.[881] Mardilovich et al. simply abraded the surface to accomplish this while Jemaa et al. used a special technique involving shot peening to attain surface pore size reduction of the stainless steel membrane, effectively creating an asymmetric membrane.[304,882] Quicker et al. used high temperature sintering to form a smoother surface for electroless plating and electrodeposition, although the resulting films were not very permselective due to macrodefects in the porous (0.5 μm) stainless steel.[436]

Jarosch et al. electrodeposited nickel and copper onto a porous Inconel support to reduce the average pore size before electroless plating, while Nam et al. decreased the average pore size of a stainless steel membrane by sintering nickel powder onto the surface and electrodepositing a layer of copper before electrodeposition of Pd–Ni.[348,859,876] This enabled the vacuum deposition of a thin hydrogen selective palladium layer of less than 1 μm onto the stainless steel support. Gryaznov et al. coated a porous stainless steel sheet with melted indium and then sputtered Pd–Ru to a thickness of 2 μm.[44] The membrane had a high flux and withstood 450 thermal cycles under hydrogen. It should be mentioned that with mechanical and chemical treatments, care must be taken to avoid weakening the surface and adversely affecting film adhesion, or actually increasing the surface roughness and pore size of the membrane.[882]

Porous ceramic supports are frequently modified with several layers to reduce the average pore size or decrease the surface roughness prior to palladium film deposition. This is usually accomplished via sol-gel or slip-cast coatings that are subsequently dried and fired. Another technique that has been used is vacuum aspiration of an alumina powder suspension through the membrane.[883] Coating porous stainless steel with an intermediate layer such as titania can also serve to reduce the pore size and result in a smoother surface more amenable to palladium deposition.[58] The surface of a membrane support can actually be too smooth. Metal films deposited onto substrates with very small pores (<20 nm) can more easily delaminate due to stress in the film or lack of mechanical interlocking with the support.[884]

### 1.5.3 Nonporous Supports

Metals, ion-conducting solids, and polymers are classified as nonporous or semi-porous supports. Their main benefit is the possibility to more easily fabricate a leak free membrane. Since the support is solid, a much thinner palladium layer can be used and discontinuities in the palladium layer will not cause defects that will result in a loss in permselectivity.[6] Advantages of metal supports include higher hydrogen permeabilities than palladium in the case of the refractory metals, and the ability to weld or braze them into a module. Disadvantages often include low hydrogen permeability in the case of ion-conducting materials such as metal oxides, and metallic interdiffusion of palladium into metallic supports at temperatures above ~400°C.[193,227,309,472]

A promising composite membrane configuration involves the deposition of a palladium layer (or foil) onto a base metal foil or tube.[6,99,193,227,309,329,332,333,449,472,885–890] Many metals other than palladium are also quite permeable to hydrogen. Relatively cheap (compared to palladium) refractory metals such as niobium, vanadium, and tantalum are an order of magnitude more permeable to hydrogen than palladium while nickel permeates hydrogen but at a slower rate than palladium (1/100 that of palladium at 600°C).[6,193,237,255,312,891–895] However, most metals are readily oxidized, impeding hydrogen dissolution into the bulk metal. A thin surface coating of palladium prevents passivation of the surface and acts as a superior catalyst for hydrogen dissociation into its atomic form.[99,197,318,326–328,333,337,896]

Unfortunately, the problem of metallic interdiffusion plagues metal–metal composite membranes. The resistance to hydrogen permeation of the metal–metal interface has not been characterized either.[193,215,338,897] Like palladium, refractory metals are susceptible to embrittlement due to high hydrogen solubility at lower temperatures.[6,332] However, compared to tantalum and niobium, vanadium seems to embrittle less.[99]

Polymers are another class of nonporous support except most are subject to limitations in operating temperature. Metallized polymers have been fabricated for hydrogen separation and reaction.[898] Mercea and coworkers studied the permselectivity enhancements from metallization of various polymers.[441,899–902] In one case, the hydrogen/nitrogen separation factor of an asymmetric cellulose acetate membrane was increased from 53 to 201 by sputter deposition of a 30 nm thick palladium layer.[441] A natural rubber layer had to be deposited between the palladium and cellulose acetate membrane to prevent damage to the cellulose acetate during sputtering. Disparities in the hydrogen permeability of the thin palladium layer from that of the bulk permeability value were ascribed to either hydrocarbon contamination, stress in the palladium, or inhibition of hydrogen recombination into molecules at the Pd/polymer interface. Apparently the polymer coatings interfered significantly with the ability of palladium to absorb/desorb hydrogen.[902]

Athayde obtained a hydrogen/carbon monoxide separation factor of 100 with poly(dimethylsiloxane) sputter coated with 250–1000 Å of $PdAg_{24}$ (atom %).[91] A polyimide toplayer protected the palladium from abrasion and a hydrogen/carbon dioxide permselectivity of 1200 was obtained at 100°C and $\Delta P = 689.5$ kPa. While flux was stable for at least 6 weeks at 25°C, impurity flux increased during repeated thermal cycles (25–100°C). Ermilova et al. evaporated a 20–80 nm $PdRu_{9.8}$ film onto a 0.15 mm thick layer of polydimethylsiloxane rubber supported on porous copper sheet. However, the hydrogen/helium separation factor was only 2.2.[903] Gryaznov reported that a 1 μm palladium alloy film magnetron sputtered onto polyarylide was hydrogen permselective and above 100°C the composite membrane had a higher hydrogen permeability than the polymer itself.[44,62,904,905] Gudeleva et al. conducted electrochemical hydrogenation of sodium p-nitrophenoxide over a cation exchange resin with a 0.4 μm palladium coating[906] and also with other palladium-containing membranes.[907]

Metals can be interdispersed within a polymer to increase the hydrogen permeability.[908] Gao et al. incorporated palladium into a poly(phenylene oxide) film that had a hydrogen/nitrogen permselectivity of up to 135.[909] The membrane was used for selectively hydrogenating cyclopentadiene at 40°C and 0.1 MPa. Fritsch and Peinemann cast polymer membranes containing nanoscale palladium, silver, and Pd/Ag particles.[910] Permselectivities were slight but the membrane was effective in decomposing nitrous oxide with hydrogen.

## 1.6 Membrane Characterization

Some of the instruments most commonly used for analyzing palladium films include scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), atomic force microscopy (AFM), X-ray diffraction (XRD), Auger-electron spectroscopy (AES), thermal desorption spectroscopy (TDS), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and electron-probe microanalysis (EPMA). These tools are indispensable for characterizing palladium membranes with respect to morphology, thickness, grainsize, and types and amounts of impurities. Membrane properties may depend on fabrication method, or result from testing history, and influence the performance of the membrane. Information gained from analysis can be used to improve fabrication and testing procedures.

AFM is useful for determining the surface roughness of a support or deposited film.[911] Souleimanova et al. used AFM to observe microstructural evolution during electroless plating to assess how osmosis influences metal film formation.[803,804] Optical microscopy of palladium membranes supported on silica has been used to visualize modes of stress induced buckling,[912,913] morphological changes during the $\alpha \rightarrow \beta$ phase transition,[914] and reflectivity indicating coating uniformity.[567] EPMA is used to measure elemental composition over cross-sections. This is useful for estimating thickness and assessing the degree of metallic interdiffusion in alloy films or interpenetration of palladium films into metallic or porous supports.[915]

The information gained from these analysis tools can be used to explain membrane performance and understand metal film formation. For example, TDS has been used to determine hydrogen binding energies and relate these to the crystallographic orientation of palladium alloy films.[212,605] XRD is used to determine grainsize, composition, and crystallographic orientation, while SEM is invaluable for observing palladium film microstructure and measuring film thickness. Combined with the appropriate software, SEM can be used to estimate the size and number of pinholes in a metal film or porous support.[902]

XPS and AES are surface techniques that can be used to determine types and concentrations of contaminants and segregation of alloying elements.[489,916–920] Either method will usually reveal a thin layer of carbon (and often oxygen, chlorine, and sulfur) on the palladium surface since palladium collects hydrocarbons from the air.[6,226,305,459,576,921–923] Depth profiling can be carried out by simultaneously sputtering the sample with ions and collecting data.[91] This is particularly useful for determining the compositional homogeneity of alloy films. Overall film composition can be measured by dissolution in acid (aqua regia is effective) and performing inductively coupled plasma emission spectroscopy (ICP).[91] Gas chromatography (GC) is useful for determining gas compositions in membrane reactor work and permeation experiments.

## 1.7 Estimation of Film Thickness

The thickness of a film is usually determined from either the weight of the deposited metal or from SEM micrographs of the film cross-section. X-ray techniques and profilometry have also been used to estimate film thicknesses.[276,567,703] From the authors' experience, calculation of the thickness by using the weight difference alone is not always accurate.[569] The deposit thickness and degree of penetration into pores can vary significantly from place to place on the substrate and sometimes large nodules (or porosity) can add (or subtract) to the thickness calculated by the weight difference method without contributing to the actual, effective thickness.[400,461,569,847,848] While these features may add increased resistance to hydrogen permeation, hydrogen might also permeate by short circuit diffusion through the thinner areas of the film. Palladium may also penetrate into the pores of a support, contributing to inaccuracies in film thickness measurements by a profilometer.[924] It is therefore suggested that film thickness be estimated by more than one method and the results averaged.

## 2. FABRICATION OF PALLADIUM COMPOSITE MEMBRANES

Palladium and palladium alloy films have been deposited by a wide variety of techniques. Electroless plating, spray pyrolysis, CVD, PVD, solvated metal atom or co-condensation deposition, impregnation, and electrodeposition have been used to fabricate palladium composite membranes.

### 2.1 Electroless Plating

Electroless plating is a prevalent form of palladium membrane fabrication because of its ease and ability to produce good results. Kikuchi and Uemiya et al., and Konno et al. were the first to create composite membranes using electroless plating, depositing thin palladium films (5–20 μm) onto porous alumina or glass supports.[180–182,866] In some cases, their membranes had infinite permselectivities and were used for various reactions.[185,186] Collins and Way deposited palladium films between 11–20 μm thick onto asymmetric alumina supports.[273,925] The membranes had high hydrogen/nitrogen selectivities (up to 1170). Shu et al. have conducted a number of studies that have contributed to knowledge on electroless plating methods (see Section Microstructural Evolution During Electroless Plating) as well as the formation of alloy membranes (see Sections Formation of Palladium Alloys and Palladium Alloy Membranes).[349,715,734,800–802,882,926–931]

Zhao et al. used vacuum infiltration to plate palladium to a thickness of 1 μm onto a palladium-modified boehmite sol-gel layer.[819] The membrane peeled during annealing in inert gas so membranes prepared using electroless plating without vacuum were tested for permeability instead. The hydrogen/nitrogen ideal separation factor was 23 at a $\Delta P$ of 1 atm and 450°C. Quicker et al. were able to most consistently produce permselective palladium films using electroless plating compared to other methods of metal deposition.[436] A $\sim 3$ μm thick film on porous (0.1 μm) ceramic had a hydrogen/nitrogen ideal separation factor of 250 at room temperature.

Huang et al. studied the permeability of 7 and 15 μm thick palladium films deposited by electroless plating onto α-alumina and supported γ-alumina supports.[270,932] By modeling the diffusion through the palladium film and the porous support, it was determined that the resistance of the support to permeation was substantial. Hsu and Buxbaum deposited palladium onto various metals and their alloys (niobium, tantalum, vanadium, and zirconium) with electroless plating to protect them from oxidation and facilitate hydrogen transport.[6,99,332,888]

### 2.2 Electroplating

Electrodeposition can be easily and swiftly carried out on a conducting substrate.[933–935] Nam et al. electroplated Pd–Ni films onto porous stainless steel supports (modified with nickel powder and electroplated copper) while evacuating the other side of the support to draw the electroplating solution through pores in the substrate and the depositing film, resulting in a permselective Pd–Ni film about 1 μm thick.[348,876] Current density was an important parameter affecting film microstructure, hydrogen permeance, and permselectivity. A hydrogen/nitrogen separation factor of $>3000$ was obtained at 450°C. Quicker et al. developed their own electroplating bath recipe for depositing palladium onto porous stainless steel.[436]

Amano et al. tested a 1.2 mm thick $V–Ni_{15}$ (atom %) alloy foil with a 0.2 μm coating of palladium deposited by pulse electroplating.[334] Below 200°C, permeability was negatively affected by surface contamination, and cracks developed at 300 kPa of pressure on the feed side. Group VB metals are also prone to hydrogen embrittlement like palladium.[332] Bryden and Ying formed nanocrystalline Pd–Fe films using pulsed electroplating that were more resistant to grain coarsening.[713]

### 2.3 Physical Vapor Deposition

Moss and Dye, and Peachey et al. studied the purification of hydrogen through Pd/Ta and Pd/V composite metal membranes.[197,227,309,339–342,936] To remove the oxide layer before sputtering, the foil was ion-milled with argon in the same chamber as the sputtering device. Palladium layers (0.1 μm) on each side of the 40 μm foil were deposited directly after cleaning by e-beam evaporation or sputtering without breaking the vacuum. Removal of the oxide layer from both sides of the refractory metal was vital to reduce diffusion resistance through the membrane. Thus, the permeability of the bare metal foil was increased ten times over its uncoated value and by a factor of 20 over the permeability of a 40 μm palladium foil. The hydrogen/helium ideal separation factor was 50,000. This high value can be expected with a metal foil where the only leaks will be at the seals and possibly along grain boundaries. The membrane was stable for 575 h at 300°C. At higher temperatures, diffusion of the palladium coating into the foil decreased the permeability.

Weirich et al. utilized Ti–Ni as a foil membrane coated with $PdCu_{40}$ alloy to protect the surface from contamination during thermochemical water splitting.[313,937,938] The addition of nickel to titanium obviated the embrittlement problem by reducing the hydrogen solubility while addition of copper to palladium prevented metallic interdiffusion between titanium and palladium since copper is much less soluble in titanium.

The primary weakness of Pd/metal composites is that as low as 400°C, metallic interdiffusion between the palladium and metal support permanently lowers membrane permeability as the palladium layer diffuses from the surface into the bulk and loses its efficacy for hydrogen dissociation.[62,193,197,313,472,801,890,897,939] This problem has been overcome by either operating at lower temperatures ($<350$°C) or incorporating a thin layer (permeable to hydrogen) between the palladium film and the metal support that acts as an impediment to metallic interdiffusion.[62,193,472,674,940,941] Also, alloying palladium with a metal that is relatively insoluble in the substrate metal can inhibit metallic interdiffusion.[313] The interface between two metals can also offer resistance to hydrogen diffusion.[328] Buxbaum and Hsu conducted a permeation study of a Pd/Zr/Pd membrane to estimate the relative resistances of the different layers to hydrogen permeation.[888]

Franz et al. have fabricated palladium micromembranes with e-beam PVD onto a perforated silicon nitride/oxide bilayer composite on a silicon wafer.[912,942,943] A hydrogen/nitrogen permselectivity of 1800 was obtained. A thin layer of titanium improved adhesion although delamination occurred when the composite membrane was pressurized from the support side. The microfabrication process enables heaters and thermocouples to be incorporated directly into the system. Such microfluidic devices may offer increased efficiency because of thermally enhanced diffusion of hydrogen towards the hot membrane.[944,945] Cui et al. produced a microreactor incorporating a 4 μm thick palladium foil for hydrogen separation during cyclohexane dehydrogenation.[946]

Mardilovich et al. sputtered tantalum and Pd–Ru onto γ-alumina membranes prepared by annealing anodic alumina discs at 897–947°C to form a nanoporous layer.[737] The 15 nm tantalum layer was to promote adhesion of the 210 nm thick Pd–Ru layer. The composite membrane permeated pure hydrogen at a rate of about 9 $mol/m^2 \cdot s \cdot Pa$ at 400°C. Quicker et al. used e-beam vaporization to deposit palladium onto porous stainless steel supports.[436] However, under the conditions they used, the films were still porous.

### 2.3.1 Magnetron Sputtering

Xomeritakis and Lin, Jayaraman and Lin, and McCool et al. have formed alloy membranes by magnetron sputtering (discussed in more detail below).[38,276,567,703,947] Jayaraman et al. sputtered palladium onto asymmetric γ-alumina supports to a thickness of 500 nm.[567] At larger thicknesses, intrinsic and interfacial shear stresses caused the film to delaminate.[567] The optimal deposition temperature of 400°C resulted in increased adhesion due to balanced intrinsic (tensile) and thermal (compressive) stresses in the film.

Bryden and Ying formed nanostructured palladium films on porous Vycor glass using magnetron sputtering to obtain a membrane with higher permeability because of increased hydrogen permeation through the grain boundaries of the nanocrystalline material.[948] Apparently there were problems with characterization of the hydrogen permeability due to pinholes and delamination of the metal layer. Basile fabricated a Pd/alumina membrane using sputtering except it was also not very permselective because it was deposited on the outside of a ceramic membrane with large pores.[695]

### 2.3.2 Ion Plating

Reactive ion plating was utilized by Meunier and Manaud to deposit nickel and palladium films onto asymmetric alumina supports.[893] First, a thin layer of $TiH_2$ (0.3 μm) was deposited to promote adhesion of the metal films deposited by ion plating under an argon atmosphere. The ion-plated metal films were porous so metal was electroplated on top. The diffusion coefficient for such a membrane with a 20 μm thick palladium film was determined at 20°C but it was destroyed by the $\alpha \rightarrow \beta$ phase transition.

## 2.4 Chemical Vapor Deposition

Ye et al. were the first to report the formation of a selective palladium composite membrane using CVD (with $PdCl_2$ as the metal source).[884] Yan et al. used cross-flow CVD to apply a thin layer of palladium within a porous α-alumina membrane by placing palladium acetate inside the tube lumen and heating to 400°C with the pressure lowered on the outside of the tube.[708,949,950] This process was repeated four times to obtain a 4.4 μm palladium film within the pores that displayed a hydrogen/nitrogen permselectivity of $>1000$. Schwartz and coworkers formed palladium films using different organometallic precursors reduced at the support surface in hydrogen gas.[117] Membrane properties were found to be sensitive to deposition temperature, as well as specific organometallic precursor.

Xomeritakis et al. and Tsapatsis et al. have deposited palladium films onto asymmetric γ-alumina supports by counter-diffusion MOCVD.[38,409,710,947] The films they obtained were quite thin (0.5–5 μm) and had some defects since helium permeated by Knudsen and viscous flow. Hydrogen/helium permselectivity was still moderately high (>200 at 300°C).[409] When palladium is deposited within the pores of the support, it has been shown to reduce embrittlement during temperature cycling.[867,951,952] Thinner palladium films ($<0.3$ μm) are also more resistant to thermocycling, possibly due to film/support interaction.[904,953,954]

Other researchers such as Meng et al. and Huang et al. have deposited palladium and Pd–Ni films onto asymmetric γ-alumina (4 nm pore size) supports using counter-diffusion MOCVD that promoted metal deposition within the pores of the membrane support.[952,955] As expected, they found that Pd–Ni alloy films (4 μm thick) were more permselective and crack-free compared to pure palladium.[607] XPS showed that no oxygen or carbon impurities were deposited in the film. Deshpande et al. deposited Pd–Ag films onto anodic γ-alumina followed by sintering of the porous deposit.[956] By using flow-through aerosol-assisted CVD, they obtained a dense crystalline film approximately 1 μm thick although some defects were present.

Thin palladium and palladium alloy films deposited by CVD often have $n$ values greater than 0.5 and closer to 1.[708] This has been attributed to surface hydrogen dissociation effects becoming more influential in the permeation process, perhaps because the films are often very thin ($<5$ μm). The increased resistance to permeation might be due to organics or other impurities trapped during deposition, although microstructure alone may account for the decreased permeability. Contamination at the grain boundaries may also inhibit hydrogen permeation.

## 2.5 Modification of Porous Supports

Researchers have taken advantage of the high surface mobility of hydrogen on palladium and have observed increased hydrogen permselectivity (greater than Knudsen) through porous ceramic, metal, and glass membranes modified with metal particles or coated with sol-gel layers containing metal salts.[62,345,417,420,422–425,957] Sol-gel layers containing metals may be deposited on macroporous supports to enhance hydrogen permselectivity by blocking defects and facilitating hydrogen surface diffusion.[408,417,420,792,819,958–960] Chai et al. increased the hydrogen permselectivities of porous alumina membranes through deposition of boehmite sols containing different metals.[345,422,423,425] Lee et al. used $H_2PdCl_4$ as the metal precursor in an alumina sol vacuum deposited into the pores of an asymmetric α-alumina support.[411,961] The pores were then modified with palladium acetate resulting in a hydrogen/nitrogen ideal separation factor of 5 at 400°C.

Deng et al. deposited boehmite sols containing palladium, platinum, copper, or nickel onto a porous alumina membrane.[417] They suggested that surface diffusion of hydrogen through membranes containing palladium or platinum was responsible for ideal separation factors greater than those expected from Knudsen diffusion, in contrast to the membranes modified with copper or nickel that adsorb hydrogen to a lesser degree and exhibited no increase in permselectivity. Uemiya et al. have reinforced this important concept by depositing various platinum group metals into the pores of alumina supports using MOCVD.[195,400,418,429,430] By partially coating the inner surfaces of pores in alumina, they determined that selective surface diffusion of spillover hydrogen plays an important role in mass transfer through the microcracks in thin and discontinuous metal films, even at high temperatures. Furthermore, by using metals other than palladium, hydrogen embrittlement was minimized. The membranes contained pores on the order of 1.6 nm and gases other than hydrogen permeated by Knudsen flow. However, hydrogen/nitrogen ideal selectivities up to 240 were obtained. Loss of hydrogen permeability upon sulfidation of the membranes lent support to the likelihood of hydrogen surface diffusion as a dominant diffusion pathway.

Zhao et al. also deposited a palladium-modified boehmite sol to form a $\gamma$-alumina layer with small pores and to activate the support for electroless deposition.[819,869,959] Pulling a vacuum on the other side of the porous support during electroless plating created a palladium film ($<1$ μm thick) that was impervious to helium at room temperature. The composite membrane had a hydrogen/nitrogen permselectivity that ranged from 20–130 at 314°C. Impregnation of a silica/alumina membrane with palladium using palladium acetate resulted in a hydrogen/nitrogen separation factor of 10 at a transmembrane pressure of 110 kPa.[408]

## 2.6 Novel Techniques

Other methods of metal film deposition have particular advantages. Spray pyrolysis, high-velocity oxy-fuel spraying (HVOF), solvated metal atom deposition (SMAD), and impregnation can be used to deposit thin films or metal particles within pores.[962] Many of these newer methods of palladium membrane fabrication require further development in order to produce thin films with the desired properties such as high permselectivity.

Li et al. deposited a Pd–Ag film onto porous alumina by spray pyrolysis of palladium and silver nitrate in a $H_2$–$O_2$ flame.[963] However, the $\sim$2 μm thick Pd–Ag film contained defects so the hydrogen/nitrogen permselectivity was 24 at 500°C. During HVOF, palladium nanoparticles are partially melted in a flame and strike the support. In this manner, Quicker et al. coated a normally difficult to plug porous stainless steel support with a permselective palladium layer, although it was relatively thick (70 μm).[436]

Basile prepared a solution of solvated palladium atoms by evaporating palladium and co-condensing it at low temperature in 1-hexene-mesitylene.[695,964] Solvated metal atom deposition (SMAD) of palladium was then carried out by warming this solution in the lumen of the porous $\gamma$-alumina support to promote coalescence of palladium on the surface. The resulting $\sim 0.1$ μm thick film initially had infinite hydrogen/nitrogen permselectivity but was not stable for more than 42 h at 322°C. The hydrogen/nitrogen permselectivity was improved (up to 8.2) by coating the membrane with another layer of palladium using the same technique.[965] Barbieri et al. also prepared a 0.1 μm film on asymmetric $\gamma$-alumina using SMAD.[399,966] However, the permselectivity of the SMAD membrane was rather low to begin with and declined further during methane steam reforming at 536°C. Vitulli et al. deposited platinum onto a porous silica/alumina support using mesitylene solvated platinum, although permeation was still primarily by Knudsen flow.[967]

Jun and Lee deposited thin palladium films using wet-impregnation deposition (reservoir method) onto porous stainless steel modified with submicron nickel particles to reduce the pore size.[915] The deposition technique involved repeated dipping in $Pd(C_3H_3)(C_5H_5)$ dissolved in pentane, drying, and reaction in hydrogen, followed by annealing under hydrogen at 550°C. The volatile nonpolar solvent helped confine the palladium layer to the surface of the support through capillary action and evaporation. For a 2 μm thick film, a hydrogen/nitrogen permselectivity of 1600 was obtained at 450°C. The film required annealing to increase its gas tightness except the palladium diffused into the nickel and stainless steel of the support if the membrane was held above 350°C. Fernandes et al. are experimenting with a unique method of metal film deposition using organometallic compounds dissolved in supercritical carbon dioxide.[968]

Kim and Lin deposited palladium inside the pores of a yttria-stabilized zirconia layer on a porous $\alpha$-alumina disk by soaking in palladium acetate dissolved in acetone, drying, and calcining.[415,858] After four cycles the palladium phase became continuous. The remaining pores were sealed using yttria/zirconia counter-diffusion CVD and the membranes were tested for oxygen permeability.[415]

## 2.7 Palladium Alloy Membranes

Preparation of palladium alloy tubes or foils has been accomplished in the past by induction melting, casting, and rolling or cold working. Harris and coworkers argon-arc melted $PdAg_{23}$ and $PdY_{7.8}$ (atom %) and homogenized the alloys in a vacuum furnace at 950°C for two weeks.[242,969] Foils were then cold-rolled, with intermediate anneals, to thicknesses of 50–100 μm. The hydrogen permeability of the Pd–Y membrane was 3.65 times the Pd–Ag membrane at 300°C and 6.8 bar differential pressure.[970] More recent work has involved the use of electroless plating, PVD, and CVD to make membranes of palladium alloys with silver, copper, gold, and nickel. Electrochemical techniques for codeposition have been developed, although successive single-metal electroless depositions followed by annealing are more common due to better alloy composition control.

To obtain a homogeneous alloy film, various researchers have used differing thermal treatment conditions for sequentially deposited metal films. Uemiya et al. annealed Pd–Ag and Pd–Cu bilayer films for 12 hours at the temperature limit of the porous glass support (500°C).[179] It was concluded that a higher temperature was needed to obtain complete alloying so subsequent Pd–Ag films were annealed above 800°C.[185] Kikuchi annealed a sequentially deposited Pd–Cu film between 300 and 540°C and a Pd–silver film between 800 and 1300°C.[172] Sakai et al. and Kawae et al. annealed Pd–Ag at 900°C for 2, and 12 hours respectively.[76,971–974] Keuler et al. annealed Pd–Ag and Pd–Ni at 650°C for 5 hours in hydrogen while Castelli et al. annealed Pd–Ag at 650°C for 5 days.[847,848,883] Temperatures above the so-called Tamman temperature [0.5 $T_m$ (K) where $T_m$ = melting point) of the lower melting point component where significant lattice migration can occur seem to be necessary to obtain homogeneity throughout the film cross-section.[801] Annealing under a hydrogen atmosphere accelerates the metallic interdiffusion process due to increased atom mobility.[293,801,915]

PVD and CVD have also been used to form alloy membranes. Meng et al. used counter diffusion CVD to deposit crack-free Pd–Ni films onto porous alumina. It has been suggested that the effects of hydrogen embrittlement may be reduced or avoided by deposition within the porous support matrix, possibly due to microporosity allowing expansion and contraction of the discrete palladium granules plugging the support pores.[708] Schwartz et al. deposited Pd–Ru alloy films onto porous alumina using CVD of palladium and ruthenium acetylacetonates, however, the resulting films were not permselective.[117] Lu and Lin looked at the deposition of Pd–Ag films using CVD of acetate-based organometallic compounds.[975] Better control over alloy composition was obtained by isolating the two precursors as opposed to premixing. A homogeneous alloy film was obtained after annealing under nitrogen at 500°C.

Xomeritakis and Lin, Jayaraman and Lin, and McCool et al. deposited Pd–Ag films onto asymmetric γ-alumina supports (3 nm pores) using magnetron sputtering.[947] The 0.16–0.55 μm films densified upon heating at 300°C and exhibited high hydrogen/helium permselectivity (up to 4000).[703] One difficulty with PVD is obtaining the desired alloy composition due to differing sputtering yields from an alloy target. This can be overcome by allowing the target surface to reach equilibrium.[703] Target equilibration before sputtering onto the porous support was crucial to obtain films with the proper composition.[276] Higher silver contents resulted in greater permselectivity by reducing the formation of microcracks caused by the stress of hydrogen absorption. Additionally, the hydrogen permeance was not inversely proportional to film thickness suggesting that hydrogen permeation was limited by processes other than diffusion through the bulk metal.[703,895] Surface reactions (or perhaps diffusion through the porous support) may have been rate limiting. Another observation regarding films deposited by magnetron sputtering was that the beginning surface roughness of the support was an important factor in obtaining a defect free and adherent membrane.

Zhao et al. also deposited thin ($<1$ μm) Pd–Ag films onto sol-gel modified alumina supports using magnetron sputtering.[869] The composite membrane had a hydrogen/nitrogen permselectivity of about 1000 at 411°C. Keeping the substrate at a high enough temperature during deposition was found to improve adhesion and higher silver concentrations increased the hydrogen/helium permselectivity (up to 3845 at 300°C) by decreasing the stress during hydride formation that opened up avenues for gas permeation. Increased hydrogen permeance was observed at larger grainsizes.

Bryden and Ying have experimented with nanocrystalline Pd–Y and Pd–Fe alloys deposited by pulsed electrodeposition and magnetron sputtering.[506,713,714,976] These alloys have better properties than pure palladium with regard to formation of the β-Pd hydride, resistance to sulfur poisoning, and increased permeability. The addition of iron and yttrium to palladium lowered the critical temperature for the $\alpha \rightarrow \beta$ phase transition and stabilized against grain growth so that the higher permeability of the nanostructured alloy material could be maintained at higher temperatures. Grain growth began in $PdFe_{20}$ and $PdY_{7.8}$ alloys (atom %) at temperatures above 400°C.[713] Even though $PdY_{7.8}$ is 3.65 times as permeable as $PdAg_{23}$ at 300°C and a pressure differential of 689.5 kPa, it was found to be prone to surface contamination.[242,970,977] Al-Shammary et al. conducted hydrogenation of ethylene on a $PdY_{7.8}$ membrane and discovered that it was easily contaminated and hydrogen, vacuum, or air could not restore the original permeability. Carbon buildup actually had a positive effect on the reaction but eventually caused the membrane to rupture.

## 2.8 Control of Film Microstructure

The importance of palladium film microstructure on composite membrane performance has been recognized and studied by many researchers in the field.[327,377,400,409,442,560,567,800,801,803,804,915,927,947,948] Work has focused on film deposition methods to control grainsize, adhesion, and film porosity. In turn, these characteristics determine membrane durability, permselectivity, and hydrogen permeability.

Shu et al. recognized that film delamination was related to stress in the film caused by the different thermal expansion coefficients of the substrate and palladium.[801] They sought to mitigate this problem by first conducting electroless plating with an electroless palladium bath that produced a more porous, stress absorbing, and well anchored layer followed by a more dense, permselective layer of palladium.[930] Jayaraman et al. found that films deposited by magnetron sputtering at room temperature peeled from the surface of the porous $\gamma$-alumina support at thicknesses greater than 300 nm. Such adhesion problems have been related to higher stresses in thicker films and defects in the surface of the porous support.[703,867] With electrodeposited films, stress decreases with increasing grainsize and the tensile stress is greatest when the film becomes continuous.[978] Using pulsed electrodeposition and magnetron sputtering, Bryden and Ying have deposited nanocrystalline palladium and Pd–Fe films with higher permeability because of a higher percentage of grain boundaries.[713,714]

## 2.9 Membrane Stability

The thermochemical/mechanical stability and hydrogen permeability of the palladium film and support determine membrane performance and usefulness. For reactions such as steam reforming or partial oxidation (POX) of methane, operation of the membrane at high temperatures ($\geq 550°C$) and pressures (>20 atm) is often required. Loss of permselectivity towards hydrogen at high temperature has been a problem with composite membranes on both porous ceramic and stainless steel supports, predominantly under dehydrogenation conditions. In some cases, decomposition of a palladium membrane was greatly accelerated by coking at temperatures above $\sim 500°C$.[199,461] Damle et al. studied the stability of various inorganic membrane materials in coal gas including a palladium foil and found that it melted above 650°C and deformed when exposed to hydrogen sulfide.[192,854] Concentrations of hydrogen sulfide as low as 1 ppm will greatly reduce the hydrogen permeability of palladium or Pd–Ag foils.[979] Operation in a catalytic fluidized bed or other abrasive environment (such as fine ash from gasified coal) may erode palladium membranes.[192,980]

Another concern is microstructural changes in the thin film of a composite membrane. The micro- and nanocrystalline grainsizes of palladium films deposited by electroless plating and other methods can be expected to sinter and conglomerate during operation at high temperature because of the thermodynamic instability due to free energy present in the large volume fraction of grain boundaries.[948,981] For example, Bryden and Ying noticed grain growth in nanocrystalline palladium at 200°C.[948] Combined with a high contact angle (poor wetting) of palladium on ceramics commonly used as supports, conglomeration and spalling with corresponding pore formation will be observed.[569,982] The palladium film is also more likely to open up where it bridges pores in a support.[304] Rate of pore formation in the thin film of a composite membrane is also proportional to thickness.[569] Höllein et al. determined that a palladium thickness of $>7$ μm was required to achieve stable and permselective operation above 400°C for a film deposited by electroless plating onto a porous alumina tube.[983] For comparison, relatively thick $\sim 20$ μm palladium films on porous stainless steel were stable up to 700°C and appeared to be indefinitely stable during long-term service under solely hydrogen or nitrogen at 450°C.[53,304] A magnesia 15% yttria membrane coated with 10 μm of $PdRu_6$ was stable at 700°C for 1000 hrs.[62] Palladium alloy films containing elements having higher melting points than palladium may extend the temperature range at which composite membranes can operate.[613]

The Sn/Pd activation/sensitization technique used prior to electroless plating may increase the defect formation rate in Pd/α-alumina composite membrane films at high temperature (>550°C).[569,984] Tin, with its low melting point, appears to cause pore formation or loosen the bond between the palladium film and the porous support. Similar membranes prepared by Quicker et al. were stable up to 620°C for at least 100 hours although pinholes formed at 850°C after only 2 hours.[436]

In the absence of reaction, simultaneous decline in hydrogen flux and increase in the flux of other gases is often observed at temperatures above $\sim 550$°C. Palladium films on porous stainless steel supports simultaneously lost hydrogen permeability while nitrogen flux increased at temperatures above 700°C.[304] While the precise mechanism for this phenomenon has not been elucidated, Yan et al. described it as sintering of the palladium grains.[949] Keuler et al. noticed agglomeration of palladium during heat treatment at 650°C.[847] Palladium sinters at temperatures as low as 200°C through grain boundary diffusion.[948] A report on platinum sintering at temperatures of 400–500°C indicated that a decrease in surface area occurred through more ordered packing of atoms in the crystal lattice and a decrease in the number of defects. With some palladium alloys, ordering at certain temperatures may increase or decrease hydrogen solubility and permeability.[40,204,306,554–566]

Often either an increase or decrease in hydrogen or nitrogen permeability is observed during the start-up period of membrane testing. Li et al. saw hydrogen flux increases through thin palladium films on porous stainless steel or α-alumina upon heating to 450°C and assumed that this was due to sintering of the palladium crystallites and reduction of a thin palladium oxide layer.[879] This presumably resulted in a decrease in the intercrystalline space, thereby enhancing hydrogen permeation. They also suggested that pinhole formation was due to impurities incorporated into the palladium film during electroless plating. Mardilovich et al. noted a hydrogen flux decrease during the first 50 hours of operation followed by stability at 350°C with ~20 μm palladium on a porous stainless steel support.[304] Speculation was that densification resulting in a loss of surface area occurred at the Pd/stainless steel interface.[304] The hydrogen flux through a Pd/Ta/Pd membrane decreased 15% over 31 days of operation at 420°C, possibly stemming from metallic interdiffusion.[6]

On porous stainless steel supports, decrease in hydrogen flux at and above 550°C has been linked to metallic interdiffusion of constituents from the stainless steel into the palladium film.[304] In contrast, palladium deposited onto hydrogen permeable dense metal supports (like vanadium or tantalum) begins to diffuse significantly at lower temperatures (around 400°C).[227,309,472] One solution to this problem is to deposit a hydrogen permeable barrier (such as alumina) between the palladium film and the metal support to inhibit metallic interdiffusion.[44,193,450,472,801,985] Coating the surface of porous stainless steel supports with TiN or tungsten (0.8 μm) prior to coating with palladium has also been effective.[62,801] Ma et al. fabricated Pd/stainless steel membranes that were stable for more than 6,000 hours at temperatures up to 450°C.

Metal deposition methods have a strong influence on membrane characteristics. Varma and coworkers invented the technique of forming palladium films under an osmotic pressure gradient where electroless plating solution and a much more concentrated solution are on opposite sides of the activated porous support.[198,803–806] In most cases they used 6 or 9 M sucrose solution. Imposing an osmotic pressure gradient promotes mass transfer to the porous surface during both surface activation and electroless plating and provides several benefits including smaller grainsize, reduction in porosity, and densification of the plated film.[803] Additionally, deeper interpenetration of the palladium film into the pores contributes to thermal stability and adherence.[198,804]

Li et al. used osmosis to plug the defects in a Pd/α-alumina composite membrane, resulting in a 10 μm thick film with a hydrogen/nitrogen permselectivity of 970.[278,986] They used a concentrated NaCl solution on the opposite side of the membrane as the electroless solution during plating. While using salt solutions created a high osmotic pressure driving force and resulted in a thinner, more dense palladium film, another report indicated that incorporation of alkaline-earth metals into the palladium film significantly reduced the hydrogen permeability.[117]

### 2.10 Alternatives to Palladium

Aside from polymers, various hydrogen separating membrane materials have been developed in the search for competitive substitutes for costly palladium.[987,988] These can be categorized as either being based on silicon (for example $SiO_2$ or SiC),[38,117,122,199,989–998] zeolites,[119,120] carbon,[116,999,1000] other metals such as nickel,[313,410,419,1001,1002] amorphous metals,[1003–1008] proton-conducting oxides,[1009–1013] or metal hydrides.[1014–1017] For example, the alloy $LaNi_5$ has a high hydrogen absorption rate and is resistant to thermal cycling.[1018,1019] Carbon membranes are selectively permeable to unsaturated hydrocarbons, carbon dioxide, or hydrogen sulfide by surface adsorption and flow, facilitating their separation from other gases such as hydrogen.[1000,1020–1024]

Nickel is a possible substitute for palladium.[488,1025] Although it is substantially less permeable, it is also a fraction of the cost. Xue and Deng fabricated an amorphous Ni–B/alumina composite membrane that had high hydrogen permeability ($\sim 3$ mol/$m^2 \cdot s$ at 250°C and $\Delta P = 250$ kPa) and the ideal separation factor for hydrogen was above the Knudsen value.[419] Vacuum was applied before and during electroless deposition to remove trapped air bubbles and facilitate penetration of the metal into the pores. Compared to a Ni–P/alumina membrane,[1026] the Ni–B film did not expand or contract during heating so the selectivity remained higher until crystallization set in above 300°C. The membrane was used in ethanol dehydrogenation.[1027] Enick et al. modeled the water–gas shift reaction taking place without catalyst at very high temperatures (>700–900°C) over a nickel/proton-conducting oxide ($BaCe_{0.80}Y_{0.20}O_3$) composite membrane.[1009] At high temperature, the equilibrium constant is small but the kinetics are fast. The membrane permeance approached that of palladium at high temperature.

Hara et al. measured the hydrogen permeability of amorphous $Zr_{36}Ni_{64}$ and although it was an order of magnitude below $PdAg_{23}$, its cost was two orders of magnitude less.[1008] Sakaguchi et al. deposited layers of $V_2O_5$, copper, and $LaCu_5$ onto polyimide films and obtained hydrogen separation factors $>100$ at 45–95°C.[1028] The membrane seemed to be resistant to carbon monoxide poisoning.

## 3. APPLICATIONS FOR PALLADIUM MEMBRANES

### 3.1 Palladium Membrane Reactors

Hydrogen is an essential feedstock in the refining and chemical industries.[78] The chief source of hydrogen is from steam reforming of light hydrocarbons such as natural gas followed by the water–gas shift reaction.[1029] Both reactions have been extensively studied both theoretically and experimentally in membrane reactors.[1009,1030–1043] Hydrogen is used for alcohol synthesis, production of ammonia and pharmaceuticals, hydrocracking, hydrotreating, Fischer–Tropsch synthesis, and for liquid-phase hydrogenations.[79,1044–1048] In a palladium membrane reactor (PMR), thermodynamically limited hydrogenation or dehydrogenation reactions can be driven towards the product side by addition or removal of hydrogen from the reactor. This translates into greater per-pass conversion, higher selectivity (restraining of side reactions), operation at lower temperature, less catalyst, smaller recycle stream, and fewer downstream separations.[4,58,157,164,168,169,176–178,195,302,461,645,877,1029,1037,1049–1060] Research on PMR's has been thoroughly covered by numerous review articles and an impressive number of studies have been reported.[30,35,41,44,46,51,55–58,62–65,68–70,163,1057,1061–1072] Gryaznov et al. and Itoh et al. have carried out a large number of experimental and theoretical studies.[4,30,44,58–62,100,101,104,106–110,112–114,139,161–164,166,168,171,210,274,292–295,444,483,487,495,496,498,502–504,566,628,645,677,691,737,862,903,904,1044,1050,1055,1057,1072–1151]

A hydrogen permselective PMR may be used to keep two streams of different phases separate. Thus a PMR can alleviate the necessity of separating the catalyst from the product in the case of liquid-phase hydrogenations such as in the production of food-grade and lubricating oils, synthetic odorants, and pharmaceuticals.[60,168,503,1072,1122,1152] A metal catalyst can be incorporated into a porous support but the membrane is not necessarily hydrogen selective. In this case the membrane serves as a three-phase contactor with reduced mass transfer resistance where the hydrogen meets the liquid inside the pores.[49,790,1071,1115,1153–1155]

Vacuum or a sweep gas can also increase the reaction rate by decreasing the hydrogen partial pressure on the permeate side, increasing the flux driving force and the permeation rate of hydrogen through the membrane.[175–177,875,965] A sweep gas may be necessary at low transmembrane pressure differentials to drive hydrogen permeation.[877] Of course using a sweep gas necessitates another separation step. Using steam as a sweep gas lessens this problem.[195,196,422,424,1156,1157] Vacuum is too expensive for most industrial applications but can be useful in experimental studies.

One way that heat can be supplied to an endothermic dehydrogenation reaction is by combusting the generated hydrogen with oxygen or carbon monoxide on the other side of the membrane.[163,165,170,171,243,271,298,333,449,872,873,888,1056,1072,1120,1130,1136,1148,1158–1168] Such reaction driven hydrogen transport through a palladium membrane is faster than diffusion into a sweep gas since the driving force for permeation is increased by making the partial pressure of hydrogen approach zero on the permeate side.[457,1127,1169–1171]

Oxidative partial dehydrogenation of isobutane has been conducted in a PMR to provide the energy for a simultaneous endothermic dehydrogenation.[1172,1173] One thing to consider when using air is that oxidation of the palladium surface may reduce permeation below 200°C.[298] Reduction of the palladium surface with hydrogen prior to reaction has been found to prevent oxidation of the membrane by sweep gas containing oxygen.[1167]

A palladium membrane may be retrofitted to an existing process to increase efficiency.[1174] This ability to augment existing equipment and debottleneck is a major plus of membrane technology.[90] A bank of palladium membranes connected ex-situ between two reactors would serve as an interstage hydrogen remover to increase yield in the second reactor.[199,1060,1175] Operating the membrane apart from the reaction zone may also reduce membrane coking.

There are particular issues associated with PMR operation that need to be addressed in order to receive industrial acceptance. For instance, predicting how existing industrial catalysts will perform in a membrane reactor may be troublesome due to the different pressure, temperature, and compositional conditions. This can influence the kinetic reaction mechanism.[1042] Either reaction kinetics or membrane permeability will determine the reaction rate in a PMR.[1176] Catalysts that are not active enough may restrict PMR performance when the rate of hydrogen permeation exceeds the rate of product formation by the catalyst. Conversely, a palladium membrane that is too thick may not have ample flux to reach the full potential of the catalyst.[172,271,449,1157] Catalysts may have to be developed specifically for PMR use to meet these challenges.

Permeability of hydrogen through palladium should be inversely proportional to film thickness so the thinner the film the faster the reaction can proceed with many thermodynamic equilibrium-limited reactions.[186,271] By reducing palladium film thickness, higher rates of conversion can be attained since the reaction is usually constrained by the permeation rate of hydrogen through the membrane and not the catalyst activity.[88,1173,1177] The rates of reaction and permeation should be evenly matched in order to operate most efficiently, so that neither thermodynamic nor kinetic limitations are encountered.[1059,1165,1178] Raybold and Huff studied oxidative dehydrogenation of isobutane to isobutylene over different catalysts.[1173] Removal of hydrogen through a palladium foil (25 or 75 μm thick) reduced the reaction temperature and improved the isobutylene yield. Due to fast reaction kinetics the performance was constrained by hydrogen extraction through the membrane. One way to estimate the degree that membrane permeation is rate-limiting is to compare the partial pressure of hydrogen in the reactor effluent to that of the permeate.[1059]

### 3.1.1 Fluidized Beds

Palladium membranes have been incorporated into fluidized beds to capitalize on the advantages of this type of reactor design.[1179] For instance, smaller catalyst particle sizes can be used to overcome diffusional limitations, and heat transfer problems in endothermic reaction systems can be improved.[1029] Adris et al. theoretically and experimentally examined methane steam reforming and proved that very high conversion (>90%) can be realized in a fluidized bed membrane reactor at the conditions of an industrial reformer.[692,1029,1157,1180] Twelve palladium membranes with 200 μm thick walls crossed the fluidized bed. The reactor was able to operate 40°C lower and with both smaller reactor and catalyst volumes than the conventional process. Increased pressure decreased conversion in the case of the fluidized bed described above because of the inadequate area of the hydrogen permeators.[692] A model by Gobina of membrane separation in a fluidized bed that produced syngas by partial oxidation of methane showed a 6.5% increase in conversion compared to the conventional process.[1179] Ostrowski et al. catalytically oxidized methane to syngas in a plug-flow reactor and a fluidized bed containing a Pd/silicalite/porous stainless steel membrane.[118]

### 3.1.2 Modeling

Mathematical modeling is a powerful tool in PMR research. Models allow the investigation of parameter spaces that are dangerous or time consuming to carry out experimentally while revealing important interelationships between variables that may not have been apparent. Model results are useful to compare against experimental results and may often be used predict performance with confidence.

Using a model, Abdalla et al. studied ethylbenzene dehydrogenation in a fluidized bed with 0.5 μm Pd/composite membranes inserted into the catalyst.[176–178,1181] High conversion was achieved (96.5%) and product selectivity was increased because hydrogen removal partially eliminated the side reaction of ethylbenzene hydrogenation to toluene.[178] Hermann et al. studied the same reaction with a 0.2 μm porous stainless steel membrane coated with 10 μm of palladium.[1165] Their model revealed that the reaction was kinetically controlled so by increasing the pressure in the PMR they increased conversion without sacrificing selectivity due to repression of side reactions through hydrogen extraction. Oxidizing the permeated hydrogen with air resulted in higher styrene yields compared to evacuation of the permeate or using an inert sweep gas. In a theoretical study of methane partial oxidation, Mleczko et al. looked at the effect on the syngas yield of a bundle of palladium tubes in a catalytic fluidized bed.[980] A simulation with a 5 μm palladium composite membrane enabled yields above the thermodynamic predictions for the feed although it was important to operate under the right hydrodynamic conditions in the bed.

Le Châtelier's principle states that for equilibrium controlled reactions, products are favored by decreased pressure when the number of moles increases during reaction.[200] However, PMR models often predict and experiments verify increased conversion resulting from higher rates of hydrogen extraction through the membranes at higher pressure.[184,1054,1157,1182] The higher the pressure, the faster the hydrogen permeates through the palladium membrane, permitting further reaction.[184] A reaction may take place at a higher pressure in a membrane reactor than in a conventional reactor with the advantage of reduced reactor volume. Methanol decomposition was enhanced by increasing pressure because of hydrogen removal from a PMR at 220°C.[1183] Methane steam reforming can be performed in a PMR at lower temperature (500°C) and higher pressure with conversions much higher than equilibrium.[172,195,1184,1185] The palladium membrane can also be used to increase the space velocity with its higher reaction rate per unit volume.[53,1184] Reduced reaction temperatures are advantageous as well. Cheaper materials can be used for reactor construction and catalysts may better resist sintering, avoid coke formation, and need to be regenerated less frequently.[42,1071,1184,1186]

Some mesoporous and microporous membranes modified with metal crystallites instead of continuous palladium films are permselective enough to increase equilibrium-limited reaction conversions above the thermodynamic limit of the feed composition.[49,417,420,422,424,863,980,1042,1187,1188] However, when permselectivity is regulated primarily by Knudsen diffusion, reactant slip to the permeate side can defeat the goal of the membrane reactor to achieve yields greater than that possible with a given reactant mixture in a normal reactor.[158,1053,1161,1189–1192] High hydrogen permselectivity is required to realize significant increase in conversion.[1064,1066,1177]

### 3.1.3 Membrane as Catalyst

In general, the relatively small surface area of the palladium membrane calls for the use of a catalyst.[1151] However, under certain circumstances, the membrane itself can be used as the catalyst and many different palladium alloys are used to catalyze specific chemical reactions. Metals or alumina have been deposited and diffused into palladium alloy films to obtain unique catalytic properties.[62,1107] For example, Gryaznov et al. interdiffused a 100 nm thick cobalt layer into $PdRu_{10}$ at 400°C for 30 min under hydrogen and the foil was used to produce alkenes from hydrogen and carbon monoxide.[62]

The PMR may couple or ‘‘conjugate’’ reactions where the hydrogen for a hydrogenation is supplied by a dehydrogenation on the opposite side of the membrane.[4, 44, 58,162–164, 166–168, 170, 171, 1051, 1123, 1129,1136,1144,1159,1160,1168,1170, 1193,1194] This has also been termed a bifunctional palladium membrane reactor.[1144] Since hydrogenations are generally exothermic, it furnishes the heat required by the dehydrogenation.[169,1144] Similarly, process streams containing hydrogen could be fed to one side of a PMR to provide the hydrogen for a hydrogenation reaction. Higher heat fluxes are required for endothermic reactions carried out in membrane reactors because of acceleration of the forward reaction, especially if the kinetics are fast.[175,1195]

Palladium membranes are used to study reaction mechanisms and kinetics because of the ability to closely control hydrogen concentration on the surface of the membrane and easily measure hydrogen production from a reaction on the palladium surface.[113,628,1104,1105,1128,1133,1176,1196–1205] Use of a palladium membrane as the catalytic surface does away with effects due to catalyst supports and intraparticle mass transfer.[1091] Such experiments are carried out electrochemically[1047,1206–1208] as well as in the gas phase.[1209] For example, through isotopic labeling of alcohols, it can be determined which hydrogens form methane, or water, or permeate through the membrane during decomposition.[453,1210,1211]

Hydrogen permeated through a palladium membrane is more reactive than molecular hydrogen adsorbed on the palladium surface and may also react more selectively in the case of incomplete hydrogenations since the surface concentration can be controlled.[4,60,113,160,594,628,1057,1072,1080,1084,1085,1097,1106, 1134,1212–1218] In fact, bringing hydrogen into the reaction space through the membrane can multiply the reaction rate relative to feeding hydrogen with the reactant mixture.[1074,1085,1202] Molecules preferentially adsorbed on the surface of the palladium film are hydrogenated by atomic hydrogen permeating through the membrane.[168,1098,1099] When hydrogen is permeated from within a metal film for a hydrogenation reaction, the permeation rate has a strong influence on preventing the formation of surface compounds that diminish the hydrogen permeability of the membrane.[1217] Once formed however, surface impurities can severely limit flux.[1198,1219] Hydrogen permeated through a palladium foil during thiophene hydrogenation inhibited sulfidation of the membrane surface.[1217]

Palladium membrane technology has the potential to hydrodesulfurize or remove contaminants from process streams more efficiently because of selective adsorption on the membrane surface.[1220] Certain molecules in a mixture can be selectively hydrogenated on a palladium membrane such as hydrocarbons with higher bond order like acetylene, ring structures, or those containing sulfur.[30,628,1097,1099,1112,1120,1212,1213,1221,1222] Selective adsorption of a particular chemical species on the membrane can be advantageous in the production of high-value-added chemicals where hydrogenation of an expensive feedstock with high selectivity is desired.[503,1109,1111,1223,1224] In addition to conserving chemicals and lowering downstream separation requirements, fewer unwanted byproducts require disposal.[271,1056] This phenomenon is explicable by the fact that less saturated molecules more easily form a $\pi$-complex during chemisorption while transfer of electron density to or from the metal depends on temperature.[919,1203,1225] The extent of adsorption of specific hydrocarbons will also depend on the palladium alloy and the hydride phase ($\alpha$ or $\beta$).[1072,1079,1103] However, sometimes the reactants or products adsorb on the membrane surface and inhibit hydrogen permeation.[504,1086] Gryaznov et al. selectively hydrogenated acetylene to ethylene in an ethylene–ethane mixture[1097] and Itoh et al. looked at the same reaction over several palladium alloys.[628] Selective hydrogenation of the triple bond in acetylenic alcohols has been accomplished in the liquid phase.[503]

Arai et al. selectively hydrogenated thiophene over a palladium membrane and found that total conversion was 5 times higher when hydrogen permeated through the membrane.[1213,1217] This is because permeated hydrogen did not have to compete with adsorption of species from the gas phase that blocked reactive sites on the surface.[1074,1201,1213,1215,1216] Activated hydrogen from within the metal can also surface diffuse or spillover to and from catalytic coatings on the palladium membrane surface.[58,200,1028,1214,1226] Edlund and Pledger used a composite membrane to remove hydrogen during the thermolysis of 0.84% hydrogen sulfide in methane at 700°C and 689.5 kPa.[449,450] The membrane consisted of a vanadium foil coated with silica, palladium, and then platinum films. Replacement of the palladium with platinum allowed operation in the presence of sulfur while the silica layer prevented metallic interdiffusion between the precious metal coatings and the vanadium foil. The membrane allowed 35% of the hydrogen sulfide to be removed from a simulated natural gas stream while loss of methane was minimal ($\leq 0.5\%$). Ammonia or chlorofluorocarbons can also be removed from gas streams in a PMR.[1227–1230]

### 3.1.4 Hydrogen Production

Various methods of methane utilization have been repeatedly studied and understandably so, given the vast reserves of natural gas that are frequently wasted due to the economics of liquefaction and transportation.[1231,1232] Furthermore, methane steam reforming is a major source of industrial hydrogen.[46,85] Kikuchi and coworkers have extensively studied this reaction using various membranes and obtained greater than equilibrium conversions at 350–550°C in a Pd/Vycor membrane.[184,195,1031] Galuszka et al. partially oxidized and dry reformed (with carbon dioxide) methane to syngas in a PMR at 350–550°C and 550–675°C respectively.[461] The membrane was a 10–15 μm thick film deposited by electroless plating onto an asymmetric α-alumina tube with 0.2 μm pores. The hydrogen/nitrogen permselectivity was close to 100%. Conversions above those predicted by equilibrium were obtained, however, severe carbon deposition was encountered that destroyed the membrane.

Garnier et al. dissociated methane over a Ru/alumina catalyst in a PMR to deposit carbon species and recover hydrogen followed by rehydrogenation of the carbon species to higher hydrocarbons.[877] The membrane lowered the conversion temperature of methane and greatly increased conversions and selectivity to ethane and propane. Surprisingly, no deactivation of either membrane or catalyst was noted. Likewise, Ishihara et al. decomposed methane over a $Ni/SiO_2$ catalyst bed around a 250 μm thick $PdAg_{10}$ tube.[1233] Reforming in PMR's for hydrogen production is discussed further in Section 3.2, The Role of Palladium Membranes in Fuel Cell Implementation.

### 3.1.5 Membrane Stability

The ability to operate a palladium membrane for extended periods of time in a given situation is essential. Therefore, comprehension of modes of change and failure is important. Adsorption of impurities as well as changes in surface chemical composition due to segregation of alloying elements may alter the permeability and catalytic properties of the palladium membrane.[211,242,444,487,496,843,916,917,919,920,926,1138,1234–1237] Grain boundary segregation of impurities can weaken palladium membranes.[50] The composition of gases in the reaction mixture can cause a particular metal to segregate to the surface, thereby changing the catalytic activity and hydrogen permeability of the membrane during operation.[502,1238,1239] Atomic ordering during operation can change the hydrogen permeability of a membrane as well.[40,204,306,554–566]

One problem is that in conventional reactors the presence of hydrogen often prevents carbon buildup and its withdrawal through the membrane causes coking of the catalyst and membrane surface, especially during exposure to unsaturated hydrocarbons.[69,192,443,474,1043,1060,1186] A higher steam to hydrocarbon ratio may be required in practice in order to avoid this problem even though studies indicate that lower steam to hydrocarbon ratios may result in equivalent performance in a membrane reactor.[175,187,1035,1037,1240] Higher steam/hydrocarbon ratios dilute the hydrogen and reduce the driving force for permeation, limiting PMR performance.[88] Simulations have shown that hydrogen removal will also increase the sulfur coverage and carbon deposition on nickel catalysts in a membrane reactor for methane steam reforming.[1241,1242] This problem may be mitigated by operating at higher temperatures and pressures while maintaining the proper ratio of components in the feed.[1041,1243]

Carbonaceous and graphitic deposits decrease membrane permeability and may also destroy the palladium film (discussed in more detail above).[242] The mechanism for this is unclear although carbon is known to be able to diffuse through the palladium lattice.[474] Even though the presence of steam in the membrane reactor can help lessen this problem, special catalyst tuning may be required for maximum PMR performance.[156,199] In one case, ethanol dehydrogenation at 350°C formed a carbonaceous layer on a palladium membrane.[1210,1211] Supplying enough oxygen to the feed to react with adsorbed carbon monoxide quelled carbon formation that inhibited hydrogen permeation.[467,1244] Steam or oxygen have been reported to have a detrimental effect on palladium membranes although there is little information published about this phenomenon.[5,432,559]

### 3.1.6 Economic Evaluations

Very high yields can be obtained in membrane reactors with appropriate operating conditions. However, to be most useful, PMR performance should be compared to industrially pertinent space velocities and throughputs of conventional processes.[70,117,271,436,1058,1059,1157,1165,1175,1178] In this regard, Criscuoli et al. overcame the equilibrium carbon monoxide conversion in a single low temperature water–gas shift reactor with a conversion of 95.3% compared to a process consisting of a high and low temperature water–gas shift reactors in series that had a conversion of 91.1%.[1042] Emonts et al. estimated that palladium films less than 1–5 μm are necessary for affordable on-board hydrogen purification[1245] while Crisciuoli et al. came up with a less stringent requirement of <20 μm for membranes to compete with industrial hydrogen production.[302] Athayde et al. estimated that the cost of a palladium membrane unit is proportional to the square of the palladium film thickness.[91] The above cost estimates do not take into account the possibility of recycling the palladium.

Aasberg-Petersen et al. conducted a feasibility study comparing the usual methane steam reformer to a membrane reactor based process.[88] They concluded that very thin (<2 μm) and completely permselective palladium membranes will be required to make membranes economically competitive with conventional processes. Temperatures of 600–650°C would also have to be employed in the membrane reactor and low electricity costs would be a prerequisite to make the obligatory recompression of the hydrogen economical. Roy et al. simulated methane steam reforming with membranes inserted into a fluidized bed.[1246] The results also indicated that a high flux (thin) membrane was imperative for the process to be feasible. The primary advantages of the fluidized bed membrane process were that it operated 225°C lower than the usual process (675 vs. 900°C), and the membranes replaced pressure swing adsorption as the means of separating hydrogen. A major disadvantage was that the pure hydrogen obtained from the membranes required energy and capital intensive recompression. The overall system including membranes took less capital and operating costs were lower than conventional methane steam reforming.

Another commercially important reaction is the dehydrogenation of ethylbenzene to styrene.[169,176–178,271,401,1047,1051,1121,1165,1181,1190,1247–1252] Using a model of ethylbenzene dehydrogenation, Abdalla et al. estimated substantial cost savings through use of a PMR with a 0.5 μm thick palladium layer.[176,177] Dittmeyer et al. predicted a 4–27% decrease in the amount of ethylbenzene required to feed a membrane reactor (3 μm palladium electroless plated onto porous α-alumina) and form the same amount of styrene produced in the conventional process.[271] They pointed out that both high membrane permeability and catalyst effectiveness are necessary for industrial use and that the membrane reactor scheme could not be rationalized based on present catalyst efficiency and membrane investment. However, Gobina and Hughes noted that the higher conversions seen in a PMR can save on the costly separation of ethylbenzene/styrene by vacuum distillation.[46]

### 3.1.7 Summary

Despite the negative aspects that must be overcome such as membrane cost and deactivation, the positive side of PMR technology includes the production of pure hydrogen, the elimination of process steps, and ultimately the conservation of energy and/or capital.[53] As a case in point, a PMR may function at lower temperatures with the same or greater selectivity and higher per-pass conversion than a conventional reactor, thus reducing the number of energy intensive separations.[158,172] Selective hydrogenation of a valuable feedstock directly to the product would minimize waste and reduce or eliminate process steps such as separation and recycle. Of course the benefits of PMR's hinge on finding ways to reduce coking and poisoning of both the catalysts and the membrane surface as well as, most importantly, development of a durable hydrogen separating membrane with a very thin palladium layer. Economic incentives exist for palladium membrane use in the chemical industry. It is hopeful that with further research they will meet the rigorous operating and cost demands.

## 3.2. The Role of Palladium Membranes in Fuel Cell Implementation

Palladium alloy composite membranes are a promising technology for integration into a reaction and/or separation process involving hydrogen generation. Palladium membranes possess high flux and permselectivity as well as the ability to operate at high temperatures and pressures. These characteristics make palladium membranes suitable for stationary and vehicular fuel cell systems. General consensus in the scientific community is that the potentially disastrous consequences of global climate change may only be remedied by curtailing the production of greenhouse gases.[1253,1254] Carbon dioxide is the primary human generated greenhouse gas of concern, due to its huge volume of emissions worldwide. Electricity production, industry, and internal combustion engines in motor vehicles constitute the largest sources of carbon dioxide produced by human activity. A PMR may assist in efficient generation of pure hydrogen from fuels for fuel cell consumption. Additionally, the carbon dioxide rich retentate from a PMR may be further compressed and injected into certain geological formations for carbon sequestration.

With the forthcoming industrialization of less developed countries, and the expanding growth of the global economy and population, the need for safe, clean, and reliable power sources will steadily increase. For instance, the automobile population is expected to double in the next 20 to 30 years, probably offsetting any gains in fuel efficiency and emission controls.[1255] Tightening of environmental laws is apt to continue with mounting pressures on natural resources and the realization of environmentally sustainable practices becomes necessary for maintenance of quality of life. It is paramount to reduce the environmental impacts associated with energy extraction and use, especially with increasing exploitation of fossil fuels.

Air pollution is an unhealthy problem in the airsheds surrounding many major cities. To reduce production of carbon dioxide and other pollutants, vehicles must be redesigned for efficiency and minimal emissions. There are a few workable prototype vehicles suitable for large-scale production that are more energy efficient and create less pollution. Energy or power is supplied from various sources including batteries, fuel cells, hydrogen, liquids derived from biomass (such as alcohols), natural gas, solar panels, and optimized internal combustion engines. Hybrid vehicles with combinations of power systems reduce emissions by burning cleaner fuels and/or making the most efficient use of fuel or energy. Hybrids that combine batteries and an internal combustion engine are currently being mass-produced by Honda and Toyota. Electric vehicles (eV's) powered solely by batteries are also becoming more prevalent with the development of storage batteries with higher energy densities.

The fuel cell vehicle is an attractive option for transportation. Fuel cells tend to be more efficient than internal combustion engines because the output is mostly electrical energy while internal combustion engines produce some mechanical power and a lot of waste heat. Hydrogen might be stored on board in the liquid or gaseous form.[1256] Gas necessitates high-pressure containment while liquid hydrogen must be stored in a cryogenic vessel. Hydrogen can also be absorbed in a hydride bed but weight, size and cost are still problems. In the latter case, intermetallic hydrides or carbon nanotubes may help to make hydrogen storage more compact and lightweight.[684,1257]

Alternatively, to provide hydrogen, a fuel would react over a catalyst bed in a PMR and purified hydrogen would be obtained through a palladium membrane.[227,340] The hydrogen would react with air in a proton-exchange membrane (PEM) fuel cell to power an electric motor. During idling, batteries could be charged for later assistance with acceleration or to supply power during the next warm-up period. Only recently have technological advancements, particularly in materials science, made the fuel cell close to being feasible for mass production. Presently, the higher cost of hydrogen or alcohols as fuels compared to gasoline as well as the cost of fuel cells limits commercialization. Development of a module for generating electricity has hinged on factors such as a durable and compact fuel cell, high yield catalysts for producing hydrogen from liquid fuels, and an effective system for preventing impurities from decreasing fuel cell performance.

PEM fuel cells (PEMFC) are lightweight, power dense, and operate at fairly low temperatures (~80°C) making them suitable for portable applications.[43] They consist of a polymer electrolyte membrane that is permeable to $H^+$ ions, sandwiched between the two electrodes. Although the amount of precious metal (platinum, palladium, or ruthenium) catalyst required within the polymer membrane has been drastically reduced, it is still a major cost of the PEM fuel cell module. Low temperature (~100°C) fuel cells that convert fuels directly into electricity are still under development. In a direct methanol fuel cell, a palladium film between the anode and cathode can prevent diffusion (or *crossover*) of methanol to the cathode.[287,1258–1260]

Pure hydrogen is the optimal fuel for the PEM fuel cell, however its distribution and storage in either the liquid or compressed gaseous form may require prohibitive capital investment. Meanwhile, expansive infrastructure already exists for liquid fuel distribution.[1261] Combined with the fact that hydrogen storage cylinders are heavy and bulky, in-situ generation of hydrogen from a liquid fuel seems to be an attractive option in the interim.[1262]

The potential applications for fuel reforming range beyond vehicular fuel-cell-based propulsion systems. Within this decade, stationary small to medium size reformer and fuel cell modules for home or business use may decentralize the power grid and provide efficient, high quality, and uninterrupted electricity. On a large scale, providing hydrogen to a fuel cell via coal gasification and purification through a palladium membrane would increase the overall efficiency of an integrated gasification combined-cycle (IGCC) coal power plant.[192,1263]

Alcohols are convenient fuels because of moderate reforming temperatures (conducive to quick start-up) and production from abundant natural gas reserves (possibly through partial oxidation) or from fermentation or gasification of plant matter and organic refuse.[360,1264–1270] Copper/zinc oxide catalysts are a promising choice for the methanol steam reforming reaction:[878,1271–1274]

$$CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2.$$

Lin and Rei obtained over 70% recovery of the hydrogen from methanol by using a PMR.[878] To improve the efficiency of the process, the unreacted methanol and hydrogen from the membrane reactor and the fuel cell were oxidized to provide heat for the reforming reaction. Such thermal integration is necessary to drive up the overall process efficiency.[1267] Careful energy management is essential for achieving high system efficiency, especially in mobile power plants.

With the proper catalyst and reaction scheme, any hydrocarbon fuel could be the source of hydrogen.[5,1269,1275] For example, Edlund has developed a fuel processor that is capable of providing hydrogen from a variety of hydrocarbons (methane, gasoline, etc.) by steam reforming.[1276] It utilizes a proprietary hydrogen separating membrane. Murata et al. produced hydrogen through ethane pyrolysis over a graphite catalyst,[1277] or decomposition of gasoline over a Ni/Ca/C catalyst,[1278] while Midilli et al. recovered hydrogen through a palladium membrane from hazelnut shells gasified by a solar collector.[1279] Dehydrogenations and cracking reactions have the advantage of no carbon monoxide generation or water handling issues (storage, steam generation, recycling).[1275,1280]

With its widespread availability, natural gas is a good choice for small and medium scale stationary fuel cell units providing decentralized (off the grid) back up or supplementary power where the waste heat from the high temperature reforming process (700°C) can be used for residential hot water or space heating.[1276] Amphlett et al. reformed diesel in a PMR.[1281] They point out that the main disadvantage of the PMR is the large pressure driving force (10–15 bar) necessary for hydrogen permeation through the membrane.[1282]

However, small amounts of unreacted fuel, unpermeated hydrogen, and the hydrogen rejected by the fuel cell can be combusted in a catalytic burner to vaporize fuel or water, and heat the reformer to provide energy for the endothermic reforming reaction.[1245,1261,1280,1283–1285]

Despite the possibility of superior efficiency, fuel cells have several drawbacks yet to be overcome. One problem for a mobile application is that fuel cells have a warm-up period and respond slowly to the need for impulse power. These problems can be alleviated by coupling with a battery or flywheel although they add weight and cost to the vehicle.[1255] An autothermal reformer combines reforming and partial oxidation.[1286] Although reforming alone may be more efficient, partial oxidation is better for providing the heat required for the endothermic reforming reaction, particularly during start-up.[1267,1269,1287] Additionally, a larger variety of hydrocarbons can be employed by using partial oxidation.[1269]

Johnson Matthey is developing an autothermal reactor called the HotSpot™ that reaches full power in less than a minute by adjusting the air/fuel ratio.[1255,1261,1262,1269] The partial oxidation and steam reforming reactions proceed on the same catalyst so that heat is transferred directly from the exothermic to the endothermic reaction while another catalyst bed removes residual carbon monoxide for PEM fuel cell use. The overall efficiency of the fuel processor/fuel cell system was 40%, which is comparable to the upper extent of internal combustion engine efficiency.[1261] Furthermore, emissions of particulates and other gaseous pollutants are miniscule or nonexistent. Arthur D. Little is working on a portable partial oxidation reactor for conversion of gasoline and air into a hydrogen rich gas for fuel cell consumption. Numerous patents have been granted for fuel reformers and many incorporate palladium membranes.[1038,1288–1303]

Another critical problem with the PEM fuel cell is that feed impurities such as sulfur compounds and carbon monoxide easily poison the fuel cell, drastically reducing power output.[227,352,457,1269] Purification of hydrogen to remove carbon monoxide to the less than 2 ppm favored for PEMFC use can be accomplished in a number of ways.[1261,1267,1269,1304,1305] These include catalytic, selective oxidation of the carbon monoxide to carbon dioxide in a preferential oxidation (PROX) reactor,[340,1267] low temperature shift of carbon monoxide and steam to hydrogen and carbon dioxide, catalytic methanation,[1269,1306] adsorption on a regeneratable getter, PSA, or membrane separation.[5,1273,1284,1307]

A permselective hydrogen separating membrane can be used to facilitate the steam reforming reaction and also prevent carbon monoxide from poisoning the fuel cell.[1267,1276] The only prerequisite is that the hydrogen generating reaction take place at high pressure to enable adequate separation through the membrane.[1245,1267,1276] A membrane reactor/hydrogen separator eliminates the need to remove carbon monoxide in a bulky PROX reactor following the reformer.[227] A hydrogen/carbon monoxide separation factor greater than 1000 is necessary to lower the carbon monoxide content of the hydrogen so that it does not reduce PEMFC performance.[1275] Other gases are excluded from the fuel cell by a palladium membrane as well, resulting in high operation efficiency. Alkaline fuel cells that are poisoned by carbon dioxide can also be supplied with membrane-purified hydrogen.

Amphlett et al. calculated that the PROX reactor required to scrub the carbon monoxide from the stream exiting the reformer is larger than the reformer, increasing the attractiveness of alternative carbon monoxide removal methods such as a palladium membrane.[1273] Plus, some loss in efficiency is incurred as some of the hydrogen is converted to water in the PROX reactor (although the catalyst is quite selective). Using a 70 μm thick Pd/Ta/Pd composite membrane, Gubler et al. purified hydrogen produced by an autothermal reformer operating at 300°C.[1287] Moss et al. purified methanol reformate through a Pd/V/Pd membrane for use in a PEM fuel cell.[197,227]

Adsorption of reactants such as carbon monoxide and water on a palladium membrane can inhibit hydrogen permeation through it under typical water–gas shift conditions ($<300°C$ and $>1$ atm).[275,332,352,454,456,1245,1308,1309] However, steam appears to adsorb more strongly than carbon monoxide at 380°C.[352] Lægsgaard Jørgensen et al. conducted methane or methanol steam reforming in a PMR at 20 atm and studied the effect of carbon monoxide on membrane reactor performance.[1037,1310] A 4 μm thick palladium composite membrane was used that had a hydrogen/nitrogen selectivity of 128 followed by a methanation reactor to further remove carbon monoxide. The overall efficiency of the methanol steam-reformer/fuel-cell power system was estimated to be 42–48%. Han et al. observed that conditions during the steam reforming of methanol reduced the hydrogen flux through a $PdCu_{40}$ membrane by $\sim 25\%$.[1285] In a membrane reactor, the catalyst can also contribute to concentration polarization that further reduces hydrogen flux through the membrane.[275]

## 3.3 Recovery and Separation of Hydrogen Isotopes

It is a general practice that hydrogen isotopes in streams used or produced in nuclear reactors and facilities are recovered and stored as metal hydrides, or oxidized, and stored on molecular sieves. Palladium membranes have been used for both recovery and separation of the three radioisotopes of hydrogen, protium ($H_2$), deuterium ($D_2$), and tritium ($T_2$) for over 40 years.[21,141,147,432,433,485,1311–1316] Tubular configurations with relatively thick walls (>100 μm) are commonly used to obtain complete separation of hydrogen isotopes from impurities. Metal membranes are also useful for extracting or injecting hydrogen into nuclear reactor coolant or fusion reactor breeder blankets.[484,1166,1317,1318] Palladium membranes are used to separate hydrogen from gas streams produced during tritium handling operations related to breeder or thermonuclear fusion reactors.[1319–1322] In fact, palladium membranes can be used as probes to measure the hydrogen concentration in a liquid or gas stream.[5,140,1323–1330] Buxbaum et al. studied the feasibility of using electroless palladium coated (2 μm on each side) zirconium tubes for extraction of tritium from the lithium-containing breeder blanket of a fusion reactor.[333,888]

The three isotopes of hydrogen (referred to here generically as ‘‘hydrogen’’) have different thermodynamic properties in metals.[416,593,1331–1342] In fact, separating the isotopes from each other using palladium and its alloys is feasible in either chromatographic columns or multi-stage cascades of membranes due to differences in solubility and diffusivity, particularly the variation in hydride dissociation pressures.[40,147,559,611,621,622,650,1343 – 1351] Depending on alloy composition and operating conditions the isotopic separation factor (ratio of hydrogen isotope fluxes through a membrane in a mixed-gas system) usually ranges between 1–2 for hydrogen/deuterium and 2–3 for hydrogen/tritium.[40,207,250,282,589,647,650,1162,1311,1334,1350,1352–1361] Larger factors have been obtained in electrochemical systems.[1362]

Extensive tests have been performed on the long-term operation of palladium alloy membranes and the effect of impurities on permeability.[1352,1353] Penzhorn et al. determined that methane poisons Pd–Ag membranes at 360°C, especially tritiated methane.[282] Air treatment at 350°C restored permeability. However, mercury (from a vacuum pump for example) can weaken and destroy palladium membranes while most other mechanical failures occur at the braze between the palladium tube and the connecting metal plumbing.[485]

Tritium decays with emission of a β-particle (electron) and a helium molecule ($^3$He). The electron can cause degradation of certain materials such as polymers and the helium can become trapped inside metals. It has been shown that during operation of palladium membranes for several years, the β-radiation has no effect but helium builds up inside the metal.[649,1353,1363,1364] Consequently, nuclear decay may not pose a problem until higher operating temperatures are used (∼400°C) where increased migration of vacancies in the metal can result in precipitation of helium bubbles that weaken the membrane.[649] In accelerated aging tests, reduced plasticity and hardening have been observed although there were no structural changes.[1365]

The fuel cycle of the International Thermonuclear Experimental Reactor (ITER) will require hydrogen recovery from the plasma exhaust gas and isotope separation.[26,27,30,485,649,1303,1366 – 1370] To maintain the proper deuterium/tritium gas composition for the fusion reaction, the isotopes will be extracted from the torus and recycled or stored while the helium waste product or ''ash'' will be vented. Pd–Ag membranes ($\sim 1\ m^2$ membrane area) are expected to recover the hydrogen isotopes while cryogenic distillation will be used to separate them from each other.[485,1371]

One scheme for hydrogen recovery from the plasma exhaust of a fusion reactor proposes to use the effect of ''superpermeability'' to facilitate hydrogen isotope transport across a metal membrane.[1372–1382] High probability of hydrogen diffusion (not necessarily high fluxes) through a metal are possible when using hyperthermal atomic hydrogen obtained by dissociation at low pressure on a hot filament or by a microwave.[215,1383] The process is highly sensitive to the surface state of the metal.[356,1378,1384–1386]

Hydrogen isotopes can be recovered from contaminated (tritiated) water in a PMR via the water–gas shift reaction,[20–22,24,28,689,1301–1303,1322,1367,1387–1390]

$$\mathrm{HTO} + \mathrm{CO} \rightarrow \mathrm{HT} + \mathrm{CO_2} (\mathrm{T} \equiv \text{tritium}).$$

A slight excess of carbon monoxide makes the $H_2O/CO$ ratio less than one to drive the conversion of water. This is assisted by hydrogen permeation through a 178 μm thick $PdAg_{23}$ membrane with vacuum on the permeate side. The relatively thick membrane is required to obtain essentially perfect selectivity for hydrogen. Tritiated water will break through if not enough carbon monoxide is used while excess results in the formation of tritiated methane that then has to be scrubbed from the effluent. A second PMR stage can also be used to further reduce the water concentration to the allowable level for environmental release. Pt/alumina catalyst is preferred because of its slow rate of carbon formation at the low $H_2O/CO$ ratios used ($<1$).[172,1035,1390] Electrolytic diffusers are also used to recover hydrogen isotopes from deuterated or tritiated water.[585,1352,1391]

### 3.4 Palladium Membranes and the Hydrogen Economy

Aside from fuel cell systems, membranes may also assist in harnessing energy from renewable sources or play a pivotal role in seasonal energy storage for the so-called hydrogen economy where hydrogen is the energy intermediate or carrier.[355,684,1059,1175,1178,1272,1279,1392–1396] Possible applications include the storage of electrical energy (from hydroelectric, wind, photovoltaic, or nuclear power) in chemical form by using a palladium membrane reactor and a reversible hydrogenation reaction or through direct production of hydrogen electrolytically from water.[5,70,145,355,826,1397] Energy would be stored during peak electrical generating times such as in the Spring when water flows are high or at night when electrical supply from power plants exceeds demand.

Membranes may become part of a system for the derivation of hydrogen from solar energy (perhaps in a solar furnace) or from thermochemical water splitting.[313,1001,1052,1398,1399] For instance, Herzog and Glaubitz obtained hydrogen from water by a metal/metal-hydride process using a $PdAg_{25}$/V/Pd–Cu membrane.[355] Hydrogen can also be recovered through pyrolysis or gasification from wastes that are typically burned such as biomass, crop residues, landfill gas, or industrial byproducts like black liquor (from paper making).[1036,1279,1400] For example, Arai et al. reacted ethanol (a product of waste fermentation) and water over a titania coated palladium foil to produce hydrogen under the illumination of a 500 W high pressure mercury lamp.[1401]

The environmental ramifications of increased energy efficiency through membrane processes include decreased reliance on non-renewable fossil fuel energy sources and a corresponding reduction in greenhouse gas emissions (carbon dioxide) and other pollutants such as nitrogen and sulfur oxides ($NO_x$ and $SO_x$). Unless hydrogen was produced from renewable sources as opposed to fossil fuels, reduction in carbon dioxide generation would come primarily from increased efficiency. In any case, the use of hydrogen as a transportation fuel (or using a hydrogen producing membrane/reformer system) would eliminate small point-source emissions of pollutants. Palladium membranes can also assist in carbon sequestration by separating hydrogen from a carbon dioxide rich stream. Carbon dioxide fixation to carbon has also been carried out directly in a palladium membrane reactor.[1402]

### 3.5 Novel Applications for Palladium Membranes

Many diverse uses for palladium membranes have been suggested. These include incorporation into a heat pump,[89,1403–1405] as a focusing injector for gas chromatography,[851,1406–1409] and for determining the hydrogen partial pressure in a gas or liquid.[5,140,1326–1330] For instance, Ford et al. measured hydrogen produced by microbes attached to the membrane surface.[1410] Heat pumps can concentrate and transfer energy from wasted heat into more useful higher temperatures. A heat pump based on reversible cyclohexane hydrogenation/dehydrogenation has been developed where the endothermic dehydrogenation extracts energy from the waste-heat stream and the exothermic hydrogenation returns the energy where it is needed at a higher temperature.[89,1403–1405] A palladium membrane increases the efficiency of the process by increasing the pressure at which the reaction can take place.[1397]

## 4. CONCLUDING REMARKS

Even as the amount of palladium in composite membranes continues to shrink, several challenges remain. Embrittlement of palladium hydrides can be overcome by the use of alloy membranes. However, the problem of coking (and other contamination) during reaction remains, as does the necessity to consistently fabricate extremely thin (and continuous) palladium films in order to decrease the capital outlay for an industrial module. Regardless of these difficulties, the promise of savings through the use of palladium composite membranes for multifunctional intensification of hydrogen separation and reaction processes warrants continued research towards a mature form of the technology.[46,1411] The outlook for this prospect is positive since each year cross-disciplinary progress is made towards thinner and longer lasting palladium membranes.

## ACKNOWLEDGMENTS

S. Paglieri gratefully acknowledges the financial support of the Advanced Materials Research Program, Office of Fossil Energy, U.S. Department of Energy for partial support of this research. Thanks to S. A. Birdsell and P. M. Brooks for helpful discussions. Thanks also to Prof. R. D. Noble of University of Colorado for patience during the preparation of this work.

## REFERENCES

1. Lorimer, D.H. Method and Apparatus for Purifying Hydrogen Gas. US Patent 5,895,519, Apr 20, 1999.
2. Roberts, P.M.; Stiles, D.A. Palladium alloy diffusion units. Platinum Met. Rev. **1969**, *13* (4), 141.
3. Hsiung, T.H.; Christman, D.D.; Hunter, E.J.; Homyak, A.R. Methane formation on $H_2$ purification using a commercial Pd–Ag membrane. AIChE J. **1999**, *45* (1), 204.
4. Gryaznov, V.M. Catalysis on permselective membranes. Dokl. Akad. Nauk SSSR **1969**, *189* (4), 755.
5. Serfass, E.J.; Silman, H. Hydrogen production and purification by the diffusion process. Chem. Eng. **1965**, *192*, CE266.
6. Buxbaum, R.E.; Kinney, A.B. Hydrogen transport through tubular membranes of palladium-coated tantalum and niobium. Ind. Eng. Chem. Res. **1996**, *35*, 530.

7. Miyazaki, J.; Kajiyama, T.; Matsumoto, K.; Fujiwara, H.; Yatabe, M. Ultra high purity hydrogen gas supply system with liquid hydrogen. Int. J. Hydrogen Energy **1996**, *21* (5), 335.
8. Lucht, J.; Hsiung, T.H.-L. Method and Apparatus for Making Ultra-pure Hydrogen. US Patent 5,955,044, Sep 21, 1999.
9. Cole, M.J. The generation of pure hydrogen for industrial applications. Platinum Met. Rev. **1985**, *25* (1), 12.
10. Berkheimer, G.D.; Buxbaum, R.E. Hydrogen pumping with palladium membranes. J. Vac. Sci. Technol. A **1985**, *3* (2), 412.
11. Bystritskii, V.M.; Dzhelepov, V.P.; Doronicheva, N.I.; Ermolov, P.F.; Oganesyan, K.O.; Omel'yanenko, M.N.; Porokhovoi, S.Y.; Rodina, A.A.; Teplov, V.E.; Fil'chenkov, V.V. Installation for obtaining ultra-pure gaseous hydrogen at a pressure of up to 50 atm. Instrum. Exp. Tech. (Prib. Tekh. Eksp.) **1972**, *15* (2), 576.
12. Sokolovskii, V.I.; Makarov, V.M. Improvement of membrane devices for the production of superpure hydrogen. Chem. Pet. Eng. (Khim. Neftegazov. Mashinostr.) **1998**, *34* (5–6), 357.
13. Young, J.R. Purity of hydrogen permeating through Pd, Pd-25% Ag, and Ni. Rev. Sci. Instrum. **1963**, *34* (8), 891.
14. Zetkin, A.S.; Guk, Y.N.; Kagan, G.E.; Levin, E.S. High-vacuum setup with mass-spectrometric attachment for studying the behavior of hydrogen in metals and alloys. Ind. Lab. (Zavod. Lab.) **1986**, *52* (5), 429.
15. Lobashina, N.E.; Savvin, N.N.; Myasnikov, I.A. Formation and transfer of hydrogen atoms from a metal activator onto the surface of the support (spillover effect) and into the gas phase. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1983**, *268* (6), 104.
16. Ketkar, S.N.; Martinez de Pinillos, J.V. In *Calibrating APIMS for* $H_2$ *Measurements Using a Palladium Purifier*, 39th Annual Technical Meeting of the Institute of Environmental Sciences, Las Vegas, Nevada, May 2–7, 1993; Institute of Environmental Sciences: 50.
17. Glazunov, G.P.; Volkov, E.D.; Baron, D.I. Study of low hydrogen flows into high-vacuum systems. Int. J. Hydrogen Energy **1999**, *24*, 829.
18. Brenna, J.T.; Tobias, H.J. Goodman, K.J. Interface System for Isotopic Analysis of Hydrogen. US Patent 5,661,038, Aug 26, 1997.
19. Villa-Aleman, E. Analysis of Hydrogen Isotope Mixtures. US Patent 5,308,979, May 3, 1994.
20. Willms, R.S.; Birdsell, S.A.; Wilhelm, R.C. Recent palladium membrane reactor development at the tritium systems test assembly. Fusion Technol. **1995**, *28*, 772.
21. Willms, R.S.; Konishi, S. Fuel cleanup systems for fusion fuel processing. Fusion Eng. Des. **1991**, *18*, 53.

22. Willms, R.S.; Wilhelm, R.; Konishi, S. Performance of a palladium membrane reactor using an Ni catalyst for fusion fuel impurities processing. Fusion Eng. Des. **1995**, *28*, 397.
23. Obara, A. Tritium Recovery Apparatus. Japan Patent JP 63175627, 1988.
24. Willms, R.S. Method for Simultaneous Recovery of Hydrogen from Water and from Hydrocarbons. US Patent 5,525,322, 1996.
25. Konishi, S.; Yoshida, H.; Naruse, Y. A design study of a palladium diffuser for a D–T fusion reactor fuel clean-up system. J. Less-Common Met. **1983**, *89* (2), 457.
26. Yamanishi, T.; Kawamura, Y.; Iwai, Y.; Arita, T.; Maruyama, T.; Kakuta, T.; Konishi, S.; Enoeda, M.; Ohira, S.; Hayashi, T.; Nakamura, H.; Kobayashi, K.; Tadokoro, T.; Nakamura, H.; Ito, T.; Yamada, M.; Suzuki, T.; Nishi, M.; Nagashima, T.; Ohta, M. Development of a tritium fuel processing system using an electrolytic reactor for ITER. Nucl. Fusion **2000**, *40* (3Y), 515.
27. Yamanishi, T.; Konishi, S.; Hayashi, T.; Kawamura, Y.; Iwai, Y.; Maruyama, T.; Kakuta, T.; O'hira, S.; Nakamura, H.; Kobayashi, K.; Nishi, M.; Nagashima, T.; Ohta, M. Demonstration of the integrated fusion fuel loop at the tritium process laboratory of the Japan Atomic Energy Research Institute. Fusion Energy **1998**, *34* (3), 536.
28. Birdsell, S.A.; Willms, R.S. Tritium recovery from tritiated water with a two-stage palladium membrane reactor. Fusion Eng. Des. **1998**, *39–40*, 1041.
29. Kammermeyer, K. Technical gas permeation processes. Chem.-Ing.-Tech. **1976**, *48* (8), 672.
30. Gryaznov, V.M. Metal containing membranes for the production of ultrapure hydrogen and the recovery of hydrogen isotopes. Sep. Purif. Methods **2000**, *29* (2), 171.
31. Koros, W.J.; Mahajan, R. Pushing the limits on possibilities for large scale gas separation: Which strategies? J. Membr. Sci. **2000**, *175*, 181.
32. Yang, W.; Xiong, G.-X. Novel porous metal/ceramic membrane materials. Curr. Opin. Solid State Mater. Sci. **1999**, *4*, 103.
33. Catalyst-membrane systems using platinum metals. Mater. Des. **1992**, *13* (6), 361.
34. Govind, R.; Atnoor, D.; Zhao, R. Future prospects and applications for metal based membranes. Key Eng. Mater. **1991**, *61 & 62*, 319.
35. Zaman, J.; Chakma, A. Inorganic membrane reactors. J. Membr. Sci. **1994**, *92*, 1.
36. Wise, E.M. *Palladium—Recovery, Properties and Uses*; Academic Press: New York, 1968.
37. Baranov, Y.M.; Stolyarova, L.V.; Shopshin, M.F.; Melik-Akhnazarov,

T.K.; Aleksashkina, T.S. Modern processes of hydrogen recovery from refinery gas. Chem. & Tech. of Fuels and Oils (Khim. Tekhnol. Topl. Masel) **1992,** *27* (5), 285.

38. Tsapatsis, M.; Gavalas, G.R.; Xomeritakis, G. *Recent Advances in Gas Separation by Microporous Ceramic Membranes*; Kanellopous, N.K., Ed.; Membrane Science and Technology Series, Elsevier: New York, 2000; Vol. 6, 397.
39. Lewis, F.A. *The Palladium Hydrogen System*; Academic Press: London, 1967.
40. Latyshev, V.V.; Bystritskiy, V.M. Interaction of hydrogen isotopes and diffusion membranes made from palladium alloys. Phys. Met. Metallogr. **1991**, *71* (6), 1.
41. Ilias, S.; Govind, R. Development of high temperature membranes for membrane reactor: An overview. AIChE Symp. Ser. **1989**, *268* (85), 18.
42. Guy, C. Membrane reactors: Possibilities of application in the petroleum and petrochemical industry. Rev. Inst. Fr. Pet. **1992**, *47* (1), 133.
43. Hägg, M.-B. Membranes in chemical processing. Sep. Purif. Methods **1998**, *27* (1), 51.
44. Gryaznov, V.M. Platinum metals as components of catalyst-membrane systems. Platinum Met. Rev. **1992**, *36* (2), 70.
45. Grashoff, G.J.; Pilkington, C.E.; Corti, C.W. The purification of hydrogen: A review of the technology emphasising the current status of palladium membrane diffusion. Platinum Met. Rev. **1983**, *27*, 157.
46. Gobina, E. Multifunctionality in chemical reactors incorporating high-temperature membrane technology. Membr. Technol. **1997**, *86*, 8.
47. Doyle, M.L. World hydrogen energy conference: Platinum metals in developing hydrogen technologies. Platinum Met. Rev. **1996**, *40* (4), 175.
48. Doyle, M.L. Membrane catalysis and the platinum group metals. Platinum Met. Rev. **1993**, *37* (3), 153.
49. Coronas, J.; Santamaría, J. Catalytic reactors based on porous ceramic membranes. Catal. Today **1999**, *51*, 377.
50. Doyle, M.L. A selective review of metal-hydrogen technology in the former U.S.S.R. Platinum Met. Rev. **1993**, *37* (2), 97.
51. Hsieh, H.P. Inorganic membrane reactors. AIChE Symp. Ser. **1988**, *261* (84), 1.
52. Mordkovich, V.Z.; Baichtock, Y.K.; Sosna, M.H. The large-scale production of hydrogen from gas mixtures: A use for ultra-thin palladium alloy membranes. Int. J. Hydrogen Energy **1993**, *18* (7), 539.
53. Ma, Y.H. Dense palladium and perovskite membranes and membrane reactors. MRS Bull. **1999**, *24* (3), 46.
54. Kikuchi, E. Hydrogen-permselective membrane reactors. CATTECH **1997**, *1* (1), 67.

55. Saracco, G.; Neomagus, H.W.J.P.; Versteeg, G.F.; van Swaaij, W.P.M. High-temperature membrane reactors: Potential and problems. Chem. Eng. Sci. **1999**, *54*, 1997.
56. Saracco, G.; Specchia, V. Catalytic inorganic-membrane reactors: Present experience and future opportunities. Catal. Rev.-Sci. Eng. **1994**, *36* (2), 305.
57. Shu, J.; Grandjean, B.P.A.; Van Neste, A.; Kaliaguine, S. Catalytic palladium-based membrane reactors: A review. Can. J. Chem. Eng. **1991**, *69* (5), 1036.
58. Gryaznov, V. Membrane catalysis. Catal. Today **1999**, *51*, 391.
59. Gryaznov, V.M. Palladium and its alloys as membrane catalysts. Kinet. Catal. **1982**, *23* (6), 1151.
60. Gryaznov, V.M. Hydrogen permeable palladium membrane catalysts. Platinum Met. Rev. **1986**, *30* (2), 68.
61. Gryaznov, V.M.; Mikhalenko, N.N.; Tarasova, V.E. The recovery of hydrogen from industrial gas mixtures by means of palladium alloy membranes. Russ. J. Phys. Chem. **1985**, *59* (10), 1534.
62. Gryaznov, V.M.; Serebryannikova, O.S.; Serov, Y.M.; Ermilova, M.M.; Karavanov, A.N.; Mischenko, A.P.; Orekhova, N.V. Preparation and catalysis over palladium composite membranes. Appl. Catal. A **1993**, *96* (1), 15.
63. Hsieh, H.P. Inorganic membrane reactors—a review. AIChE Symp. Ser. **1989**, *268* (85), 53.
64. Saracco, G.; Versteeg, G.F.; van Swaaij, W.P.M. Current hurdles to the success of high-temperature membrane reactors. J. Membr. Sci. **1994**, *95*, 105.
65. Uemiya, S. State-of-the-art of supported metal membranes for gas separation. Sep. Purif. Methods **1999**, *28* (1), 51.
66. Armor, J.N. Catalysis with permselective inorganic membranes. Appl. Catal. **1989**, *49*, 1.
67. Armor, J.N. Challenges in membrane catalysis. CHEMTECH **1992**, *22*, 557.
68. Armor, J.N. Membrane catalysis: Where is it now, what needs to be done? Catal. Today **1995**, *25* (3–4), 199.
69. Armor, J.N. Applications of catalytic inorganic membrane reactors to refinery products. J. Membr. Sci. **1998**, *147*, 217.
70. Armor, J.N. The multiple roles for catalysis in the production of $H_2$. Appl. Catal. A **1999**, *176* (2), 159.
71. Sherwood, T.K. Hydrogen Separation Apparatus. US Patent 3,407,571, 1968.
72. Straschil, H.K.; Lopez, T.C. Diffusion Purification of Gases. US Patent 3,238,703, 1966.

73. Najjar, M.S.; Dorawala, T.G.; Koturk, U. Membrane and Separation Process. US Patent 5,358,553, Oct. 25, 1994.
74. Jain, R.; Whitlock, W.H. Recovery of Noble Gases. EP Patent 0826629, 1998.
75. Davidson, A.P. Membranes. WO Patent 9009231, Aug 23, 1990.
76. Sakai, N.O.; Takahashi, C.T.; Abe, T.K.; Fujii, N.T. Connected Body Comprising a Gas Separator and a Metal, and Apparatus for Separating Hydrogen Gas from a Mixed Gas. US Patent 5,518,530, May 21, 1996.
77. Foley, R.J.; Snuttjer, O.R. Generator Hydrogen Purge Gas Economizer with Membrane Filter. US Patent 6,126,726, Oct 3, 2000.
78. Ramachandran, R.; Menon, R.K. An overview of industrial uses of hydrogen. Int. J. Hydrogen Energy **1998**, *23* (7), 593.
79. Docekal, J. Hydrogen production from hydrocarbons. Int. J. Hydrogen Energy **1986**, *11* (11), 709.
80. Philpott, J.E. Hydrogen diffusion technology: Commercial applications of Pd membranes. Platinum Met. Rev. **1985**, *29* (1), 12.
81. Scholz, W.H. Processes for industrial producation of hydrogen and associated environmental effects. Gas Sep. Purif. **1993**, *7* (3), 131.
82. Matlack, G.L. A fully integrated hydrogen diffusion system. Platinum Met. Rev. **1969**, *13* (1), 26.
83. Production of ultra-pure hydrogen. Platinum Met. Rev. **1964**, *8* (3), 91.
84. Matlack, G.L. Ultrapure hydrogen in metal processing. Met. Prog. **1964**, *85* (3), 114.
85. Adris, A.M.; Pruden, B.B.; Lim, C.J.; Grace, J.R. On the reported attempts to radically improve the performance of the steam methane reforming reactor. Can. J. Chem. Eng. **1996**, *74*, 177.
86. Philpott, J.E. The on-site production of hydrogen. Platinum Met. Rev. **1976**, *20* (4), 110.
87. Catalytic hydrogen. Processing **1982**, *28* (October), 47.
88. Aasberg-Petersen, K.; Nielsen, C.S.; Jørgensen, S.L. Membrane reforming for hydrogen. Catal. Today **1998**, *46*, 193.
89. Cox, K.E. In *Irreversibility Analysis of Hydrogen Separation Schemes in Thermochemical Cycles*, Proc. 2nd World Hydrogen Energy Conf., Zurich, Switzerland, 1978; Veziroglu, T.N., Seifritz, W., Eds.; Pergamon Press: Elmsford, New York; 471.
90. Meindersma, G.W.; Kuczynski, M. Implementing membrane technology in the process industry: Problems and opportunities. J. Membr. Sci. **1996**, *113*, 285.
91. Athayde, A.L.; Baker, R.W.; Nguyen, P. Metal composite membranes for hydrogen separation. J. Membr. Sci. **1994**, *94*, 299.
92. Ho, W.S.W.; Sirkar, K.K. *Membrane Handbook*; Van Nostrand Reinhold: New York, 1992.

93. Mordkovich, V.Z.; Baichtock, Y.K.; Sosna, M.H. The large scale production of hydrogen from gas mixtures. Platinum Met. Rev. **1992**, *36* (2), 90.
94. Fleming, G.K.; Dupuis, G.E. Hydrogen membrane recovery estimates. Hydrocarbon Process. **1993** (April), *72*, 61.
95. McBride, R.B.; McKinley, D.L. A new hydrogen recovery route. Chem. Eng. Prog. **1965**, *61* (3), 81.
96. McCaffrey, R.R.; McAtee, R.E.; Grey, A.E.; Allen, C.A.; Cummings, D.G.; Appelhans, A.D.; Wright, R.B.; Jolley, J.G. Inorganic membrane technology. Sep. Sci. Technol. **1987**, *22* (2 and 3), 873.
97. Labrune, D.; Limacher, B.; Guidon, H.; Moll, G. Separation of hydrogen isotopes from nitrogen with polyimide membrane. Fusion Technol. **1995**, *28*, 676.
98. Britan, L.M.; Leites, I.L. Analysis of the efficiency of various designs of membrane gas separation units. Sov. Chem. Ind. (Khim. Prom-st.) **1990**, *22* (10), 61.
99. Buxbaum, R.E.; Marker, T.L. Hydrogen transport through non-porous membranes of palladium-coated niobium, tantalum and vanadium. J. Membr. Sci. **1993**, *85*, 29.
100. Pallegedara, A.B.; Gul'yanova, S.G.; Gryaznov, V.M.; Vedernikov, V.I.; Starkovskii, N.I. Mutual influence of ethylene and ammonia on their adsorption and on the efficiency of oxidation by oxygen diffusion through silver. Russ. J. Phys. Chem. **1995**, *69* (9), 1493.
101. Pallegedara, A.B.; Gul'yanova, S.G.; Vedernikov, V.I.; Gryaznov, V.M.; Starkovkskii, N.I. Oxygen permeability of thin silver membranes: III. Oxidation of ammonia on a silver membrane catalyst. Chem. Kinet. Catal. **1994**, *68* (5), 805.
102. Mullhaupt, J.T. Oxygen Permeable Membranes. US Patent 3,359,705, 1967.
103. Wu, D.; Outlaw, R.A.; Ash, R.L. Glow-discharge enhanced permeation of oxygen through silver. J. Appl. Phys. **1993**, *74* (8), 4990.
104. Vedernikov, V.I.; Gul'yanova, S.G.; Gryaznov, V.M. Reactions of ammonia and of ethanol vapour with oxygen diffusing through a silver membrane catalyst. Russ. J. Phys. Chem. **1984**, *58* (1), 155.
105. Nogerbekov, B.Y.; Fogel', L.A.; Sokol'skii, D.V. The mechanism of the hydrogenation of benzoquinone on a palladium–silver membrane catalyst. Russ. J. Phys. Chem. **1988**, *62* (7), 1006.
106. Gul'yanova, S.G.; Gryaznov, V.M.; Yagodovskii, V.D.; Gakhardo, P.; Suluarivelo, L.; Rusinova, G.V. Adsorption and oxidation of piperylene on silver. Kinet. Catal. **1977**, *18* (1), 160.
107. Gul'yanova, S.G.; Kolosov, E.N.; Starkovskii, N.I.; Vedernikov, V.I.; Gryaznov, V.M. Oxygen permeability of thin silver membranes. II.

Effect of the adsorption of toluene on the transport of oxygen through silver. Russ. J. Phys. Chem. **1989**, *63* (10), 1478.

108. Gul'yanova, S.G.; Vedernikov, V.I.; Gryaznov, V.M. The permeability to oxygen of a silver membrane with a layer of silver on its outlet surface. Russ. J. Phys. Chem. **1977**, *51* (1), 98.
109. Gryaznov, V.M.; Vedernikov, V.I.; Gul'yanova, S.G. Participation of oxygen, having diffused through a silver membrane catalyst, in heterogeneous oxidation processes. Kinet. Catal. **1986**, *27* (1), 129.
110. Gryaznov, V.M.; Smirnov, V.S.; Gul'yanova, S.G.; Ermilova, M.M. Conversions of ethylene on a silver membrane catalyst. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1976**, *25* (3), 490.
111. Anshits, A.G.; Shigapov, A.N.; Vereshchagin, S.N.; Shevnin, V.N. Oxidative conversion of methane into $C_2$ hydrocarbons on silver membrane catalysts. Kinet. Catal. **1989**, *30* (5), 1103.
112. Kurina, L.N.; Plakidkin, A.A.; Gul'yanova, S.G.; Vedernikov, V.I.; Gryaznov, V.M. The combined oxidation of methanol and ethanol on silver catalysts. Dokl. Akad. Nauk SSSR **1985**, *281* (4), 358.
113. Gryaznov, V.M.; Gul'yanova, S.G.; Serov, Y.M. The role of the adsorbed forms of hydrogen and oxygen in the reaction of oxygen-containing one-carbon molecules on membrane catalysts. Russ. Chem. Rev. (Usp. Khim.) **1989**, *58* (1), 35.
114. Kolosov, E.N.; Gryaznov, V.M.; Starkovskii, N.I. Mass-spectrometric study of the permeation of oxygen through a silver membrane catalyst during oxidation reactions. Russ. J. Phys. Chem. **1977**, *51* (9), 1318.
115. Yan, Y.; Davis, M.E.; Gavalas, G.R. Preparation of zeolite ZSM-5 membranes by in-situ crystallization of porous $\alpha$-$Al_2O_3$. Ind. Eng. Chem. Res. **1995**, *34*, 1652.
116. Tsapatsis, M.; Gavalas, G.R. Synthesis of porous inorganic membranes. MRS Bull. **1999**, *24* (3), 30.
117. Schwartz, R.W.; Collins, J.P.; Ng, M.F.; Brinker, C.J.; Ward, T.L.; Sehgal, R.; Xia, C.; Udovich, C.A.; Masin, J.; Hagen, G.P. Inorganic Membrane Reactor Technology CRADA #1176. In *Final Report and Assessment of Membrane Technology, SAND97-0949*; Sandia National Laboratory, 1997.
118. Ostrowski, T.; Giroir-Fendler, A.; Mirodatos, C.; Mleczko, L. Comparative study of the partial oxidation of methane to synthesis gas in fixed-bed and fluidized-bed membrane reactors. Part II—development of membranes and catalytic measurements. Catal. Today **1998**, *40*, 191.
119. Casanave, D.; Ciavarella, P.; Fiaty, K.; Dalmon, J.-A. Zeolite membrane reactor for isobutane dehydrogenation: Experimental results and theoretical modelling. Chem. Eng. Sci. **1999**, *54*, 2807.

120. Ciavarella, P.; Moueddeb, H.; Miachon, S.; Fiaty, K.; Dalmon, J.-A. Experimental study and numerical simulation of hydrogen/isobutane permeation and separation using MFI-zeolite membrane reactor. Catal. Today **2000**, *56*, 253.
121. Geus, E.R.; den Exter, M.J.; van Bekkum, H. Synthesis and characterization of zeolite (MFI) membranes on porous ceramic supports. J. Chem. Soc., Faraday Trans. **1992**, *88* (20), 3101.
122. Noble, R.; Falconer, J. Silicalite-1 zeolite composite membranes. Catal. Today **1995**, *25* (3–4), 209.
123. Thomas, C.E.; Kuhn, I.F., Jr.; James, B.D.; Lomax, F.D., Jr.; Baum, G.N. Affordable hydrogen supply pathways for fuel cell vehicles. Int. J. Hydrogen Energy **1998**, *23* (6), 507.
124. Hughes, R.C.; Schubert, W.K.; Buss, R.J. Solid-state hydrogen sensors using palladium–nickel alloys: Effect of alloy composition on sensor response. J. Electrochem. Soc. **1995**, *142* (1), 249.
125. Ali, J.K.; Baiker, A. Measuring conversion in dehydrogenation reactions with the aid of a Pd–Ag membrane. Ind. Eng. Chem. Res. **1995**, *34*, 3166.
126. Juda, W.; Frant, M.S. Method of Operating a Fuel Cell Comprising a Hydrogen Diffusion Otherwise Impermeable Anode. US Patent 3,423, 244, Jan. 21, 1969.
127. Hartner, A.J.; Vertes, M.A. Fuel Cell Comprising a Hydrogen Diffusion Anode Having Two Layers of Dissimilar Metals and Method of Operating Same. US Patent 3,393,098, Jul. 16, 1968.
128. Oswin, H.G. Non-porous Hydrogen Diffusion Fuel Cell Electrodes. US Patent 3,092,517, 1963.
129. Oswin, H.G.; Chodosh, S.M. *Nonporous Hydrogen Depolarized Anode for Fuel Cells*; Young, G.J., Linden, H.R., Eds.; Advances in Chemistry Series, American Chem. Soc: New York, 1965; Vol. 47, 61.
130. Otero, T.F.; Bireben, M.T. In *Hydrogen Electrode for Fuel Cell*, 2nd Intl. Symp. on New Materials for Fuel Cells and Modern Battery, Montreal, Quebec, Canada, July 6–10, 1997; Savadogo, O., Roberge, P.R., Eds.; Ecole Polytech: Montreal, 894.
131. Hockaday, R. Small compact and portable fuel cell systems. Platinum Met. Rev. **1998**, *42* (3), 115.
132. Hockaday, R.G. Surface Replica Fuel Cell for Micro Fuel Cell Electrical Power Pack. US Patent 5,759,712, 1998.
133. Greene, N.D.; Cleary, H.J. Fuel Cells: Palladium Hydrogen Diffusion Electrode. US Patent 3,497,390, Feb. 24, 1970.
134. Kordesch, K. The advancement of fuel cell systems and spin-off battery technology. Ber. Bunsen-Ges. **1990**, *94*, 902.

135. Connor, H. Palladium alloy diffusion cells. Platinum Met. Rev. **1962**, *6* (4), 130.
136. Brogden, D. Method of Making a Thin Gas Diffusion Membrane. US Patent 3,505,180, Apr. 7, 1970.
137. Antler, M. The development and application of palladium contact materials. Platinum Met. Rev. **1987**, *31* (1), 13.
138. Fleischmann, M.; Pons, S. Electrochemically induced nuclear fusion of deuterium. J. Electroanal. Chem. **1989**, *261*, 301.
139. Gryaznov, V.M. Contribution of A.V. Frost to the investigation of catalytic processes of hydro- and dehydrogenation. Russ. J. Phys. Chem. **1996**, *70* (9), 1443.
140. Graham, T. Absorption and separation of gases by colloid septa. Philos. Trans. R. Soc. **1866**, *156* (399), 426.
141. Darling, A.S. The diffusion of hydrogen through palladium. Platinum Met. Rev. **1958**, *2* (1), 16.
142. Snelling, W.O. Apparatus for Separating Gases. US Patent 1,174,631, Mar. 7, 1916.
143. Hunter, J.B. Large Surface Area Hydrogen Permeation Cell. US Patent 2,961,062, Nov. 22, 1960.
144. DeRosset, A.J. Diffusion of hydrogen through palladium membranes. Ind. Eng. Chem. **1960**, *52* (6), 525.
145. Darling, A.S. Thermal and electrolytic palladium alloy diffusion cells: Complementary methods of obtaining ultra-pure hydrogen. Platinum Met. Rev. **1963**, *7* (4), 126.
146. Cohn, J.G.E. Hydrogen Diffusion Process. US Patent 3,238,700, Mar. 8, 1966.
147. Ackerman, F.J.; Koskinas, G.J. A model for predicting the permeation of hydrogen–deuterium–inert gas mixtures through palladium tubes. Ind. Eng. Chem. Fundam. **1972**, *11* (3), 332.
148. Grashoff, C.J.; Pilkington, C.E.; Court, C.W. The purification of hydrogen. Platinum Met. Rev. **1960**, *4*, 130.
149. Hunter, J.B. Ultra-pure hydrogen by diffusion through palladium. Abstr. Pap.-Am. Chem. Soc. **1963**, *145*, 12S.
150. Anonymous Palladium alloy diffusion process for hydrogen purification. Platinum Met. Rev. **1962**, *6* (2), 47.
151. Hunter, J.B. Silver–Palladium Film for Separation and Purification of Hydrogen. US Patent 2,773,561, Dec. 11, 1956.
152. Cohn, G.; Straschil, H.K. The role of platinum metals in the purification of hydrogen. Abstr. Pap.-Am. Chem. Soc. **1963**, *145*, 11S.
153. King, L.D.P.; Baker, C.P.; Schreiber, R.E. Hydrogen Purification System. US Patent 2,536,610, Jan. 2, 1951.
154. Gol'tsov, V.A.; Kagan, G.E.; Gel'd, P.V. Apparatus for the study of

coefficients of diffusion, penetrability, and solubility of hydrogen and deuterium in metals (exchange of experience). Ind. Lab. (Zavod. Lab.) **1971**, *37* (6), 949.

155. Betteridge, W.H.; Hope, J. The separation of hydrogen from gas mixtures. Platinum Met. Rev. **1975**, *19*, 50.
156. Raich, B.A.; Foley, H.C. Supra-equilibrium conversion in palladium membrane reactors: kinetic sensitivity and time dependence. Appl. Catal. A **1995**, *129*, 167.
157. Mohan, K.; Govind, R. Analysis of equilibrium shift in isothermal reactors with a permselective wall. AIChE J. **1988**, *34* (9), 1493.
158. Mohan, K.; Govind, R. Effect of temperature on equilibrium shift in reactors with a permselective wall. Ind. Eng. Chem. Res. **1988**, *27*, 2064.
159. Wood, B.J. Dehydrogenation of cyclohexane on a hydrogen-porous membrane. J. Catal. **1968**, *11*, 30.
160. Wood, B.J.; Wise, H. The role of adsorbed hydrogen in the catalytic hydrogenation of cyclohexene. J. Catal. **1966**, *5* (1), 135.
161. Gryaznov, V.M. Mechanism of the catalytic redistribution of hydrogen in unsaturated cyclic hydrocarbons. Russ. Chem. Rev. (Usp. Khim.) **1963**, *32* (4), 188.
162. Gryaznov, V.M. Conjugation of reactions using membrane catalysts. Kinet. Catal. **1971**, *12* (3), 564.
163. Gryaznov, V.M.; Smirnov, V.S. The reactions of hydrocarbons on membrane catalysts. Russ. Chem. Rev. (Usp. Khim.) **1974**, *43* (10), 821.
164. Gryaznov, V.M.; Smirnov, V.S.; Ivanov, L.K.; Mishchenko, A.P. Coupling of reactions promoted by hydrogen transfer through the catalyst. Dokl. Akad. Nauk SSSR **1970**, *190* (1), 144.
165. Pfefferle, W.C. Process for Dehydrogenation. US Patent 3,290,406, Dec. 6, 1966.
166. Basov, N.L.; Gryaznov, V.M. Dehydrogenation of cyclohexanol and hydrogenation of phenol into cyclohexanone on a membrane catalyst produced from a palladium–ruthenium alloy. Chem. Abstr. **1987**, *107*, 236107u.
167. Li, J.; Mau, A.W.-H.; Strauss, C.R. The use of palladium on porous glass for catalytic coupling reactions. Chem. Commun. **1997**, *14*, 1275.
168. Gryaznov, V.M.; Smirnov, V.S.; Slin'ko, M.G. The development of catalysis by hydrogen-porous membranes. Stud. Surf. Sci. Catal. **1981**, *7A*, 224.
169. Moustafa, T.M.; Elnashaie, S.S.E.H. Simultaneous production of styrene and cyclohexane in an integrated membrane reactor. J. Membr. Sci. **2000**, *178*, 171.

170. Orekhova, N.V.; Basov, N.L.; Ermilova, M.M.; Gryzanov, V.M. Conjugation of reactions producing and consuming hydrogen on catalyst-membrane systems. Russ. J. Phys. Chem. **1993**, *68* (12), 1944.
171. Itoh, N.; Wu, T.-H. An adiabatic type of palladium membrane reactor for coupling endothermic and exothermic reactions. J. Membr. Sci. **1997**, *124*, 213.
172. Kikuchi, E. Palladium/ceramic membranes for selective hydrogen permeation and their application to membrane reactor. Catal. Today **1995**, *25* (3–4), 333.
173. Uemiya, S.; Koike, I.; Kikuchi, E. Promotion of the conversion of propane to aromatics by use of a palladium membrane. Appl. Catal. **1991**, *76*, 171.
174. Chmielewski, D.; Ziaka, Z.; Manousiouthakis, V. Conversion targets for plug flow membrane reactors. Chem. Eng. Sci. **1999**, *54*, 2979.
175. Madia, G.S.; Barbieri, G.; Drioli, E. Theoretical and experimental analysis of methane steam reforming in a membrane reactor. Can. J. Chem. Eng. **1999**, *77* (4), 698.
176. Abdalla, B.K.; Elnashaie, S.S.E.H. A membrane reactor for the production of styrene from ethylbenzene. J. Membr. Sci. **1993**, *85*, 229.
177. Abdalla, B.K.; Elnashaie, S.S.E.H. Catalytic dehydrogenation of ethylbenzene to styrene in membrane reactors. AIChE J. **1994**, *40* (12), 2055.
178. Abdalla, B.K.; Elnashaie, S.S.E.H. Fluidized bed reactors without and with selective membranes for the catalytic dehydrogenation of ethylbenzene to styrene. J. Membr. Sci. **1995**, *101*, 31.
179. Uemiya, S.; Sato, N.; Ando, H.; Kude, Y.; Matsuda, T.; Kikuchi, E. Separation of hydrogen through palladium thin film supported on a porous glass tube. J. Membr. Sci. **1991**, *56*, 303.
180. Uemiya, S.; Kude, Y.; Sugino, K.; Sato, N.; Matsuda, T.; Kikuchi, E. A palladium/porous-glass composite membrane for hydrogen separation. Chem. Lett. **1988**, 1687.
181. Kikuchi, H. Medium for Separating Hydrogen. JP Patent 62273029, 1987.
182. Kikuchi, H. Preparation of Hydrogen Separating Medium. JP Patent 62273030, 1987.
183. Kikuchi, H. Film for Separating Hydrogen and Production thereof. JP Patent 63294925, 1988.
184. Uemiya, S.; Sato, N.; Ando, H.; Matsuda, T.; Kikuchi, E. Steam reforming of methane in a hydrogen-permeable membrane reactor. Appl. Catal. **1991**, *67*, 223.
185. Uemiya, S.; Matsuda, T.; Kikuchi, E. Hydrogen permeable palladium–

silver alloy membrane supported on porous ceramics. J. Membr. Sci. **1991**, *56*, 315.

186. Uemiya, S.; Matsuda, T.; Kikuchi, E. Aromatization of propane assisted by palladium membrane reactor. Chem. Lett. **1990**, 1335.
187. Uemiya, S.; Sato, N.; Ando, H.; Kikuchi, E. The water gas shift reaction assisted by a palladium membrane reactor. Ind. Eng. Chem. Res. **1991**, *30*, 585.
188. Uemiya, S.; Sasaki, H.; Matsuda, T.; Kikuchi, E. Preparation of thin palladium films by use of an electroless plating technique. J. Chem. Soc. Jpn. (Nippon Kagaku Kaishi) **1990**, *6*, 669.
189. Abe, F. Separating Membrane of Hydrogen Gas. JP Patent 62121616, 1987.
190. Swanson, M.L. *Energy and Environmental Research Emphasizing Low-rank Coal-task 3.10: Gas Separation and Hot-gas Cleanup, DE-FC21-93MC30097*; DOE, 1995.
191. Hurley, J.P.; McCollor, D.P. *Materials for Gas Separation and Hydrogen Separation Membranes: Semi-annual Report, DE00001680*; Federal Energy Technology Center (FETC): Morgantown, West Virginia, US: Energy and Environmental Res. Cntr., Grand Forks, North Dakota, US, 1997.
192. Damle, A.S.; Lau, K.H.; Wood, B.J.; Sanjurjo, A.; Krishnan, G.N. *Thermal and Chemical Degradation of Inorganic Membrane Materials, DE96000598*; SRI International: Menlo Park, California, US, 1995.
193. Edlund, D.; Friesen, D.; Hohnson, B.; Pledger, W. Hydrogen-permeable metal membranes for high-temperature gas separations. Gas Sep. Purif. **1994**, *8* (3), 131.
194. Dowdy, T.E. Coal Gasification and Hydrogen Production System and Method. US Patent 5,955,039, Sep. 21, 1999.
195. Kikuchi, E. Membrane reactor application to hydrogen production. Catal. Today **2000**, *56* (1–3), 97.
196. Ohta, Y.; Gondaira, M.; Kobayashi, K.; Fujimoto, Y.; Kuroda, K. Study on the performance of a steam reformer of town gas equipped with palladium membrane. AIChE Annual Meeting, San Francisco **1994**, *198* (76i).
197. Dye, R.C.; Birdsell, S.A.; Snow, R.C.; Moss, T.S.; Peachey, N. *Advancing the Technology Base for High-temperature Membranes, DE98000093*; Los Alamos National Laboratory: Los Alamos, New Mexico, US, 1997.
198. Yeung, K.L.; Aravind, R.; Szegner, J.; Varma, A. Metal composite membranes: synthesis, characterization and reaction studies. Stud. Surf. Sci. Catal. **1996**, *101*, 1349.
199. Collins, J.P.; Schwartz, R.W.; Sehgal, R.; Ward, T.L.; Brinker, C.J.;

Hagen, G.P.; Udovich, C.A. Catalytic dehydrogenation of propane in hydrogen permselective membrane reactors. Ind. Eng. Chem. Res. **1996**, *35* (12), 4398.

200. Foley, H.C.; Wang, A.W.; Johnson, B.; Armor, J.N. Effect of a model hydrogenation on a catalytic palladium membrane. ACS Symp. Ser. **1993**, *517*, 168.
201. Völkl, J.; Alefeld, G. Hydrogen in Metals—II. In *Topics in Applied Physics*; Springer-Verlag: New York, 1978; Vol. 29.
202. *Hydrogen in Metals I: Basic Properties*; Alefeld, G., Völkl, J., Eds.; Springer-Verlag: New York, 1978; Vol. 28.
203. Timofeyev, N.I.; Berseneva, F.N.; Gromov, V.I. Changes in the mechanical properties of palladium and its alloys with silver on exposure to hydrogen. Phys. Met. Metallogr. **1981**, *51* (2), 159.
204. Gol'tsov, V.A.; Timofeev, N.I.; Kagan, G.E.; Aizenbud, M.B.; Baichtok, Y.K. Hydrogen permeability and hydrogen resistance of some palladium alloys. Sov. Mater. Sci. (Fiz.-Khim. Mekh. Mater.) **1973**, *9* (5), 534.
205. Maruno, T.; Tsuji, H.; Otsuka, R. Hydrogen embrittlement of Pd–Ag binary alloys. J. Jpn. Inst. Met. **1983**, *47* (9), 768.
206. Feenstra, R.; de Groot, D.G.; Griessen, R.; Burger, J.P.; Menovski, A. Absorption of hydrogen in Pd–Co and Pd–U alloys. J. Less-Common Met. **1987**, *130*, 375.
207. Maeland, A.; Flanagan, T.B. Lattice constants and thermodynamic parameters of the hydrogen–platinum–palladium and deuterium–platinum–palladium systems. J. Phys. Chem. **1964**, *68* (6), 1419.
208. Roshan, N.R.; Parfenova, N.L.; Polyskova, V.P.; Savitsky, E.M.; Mischenko, A.P.; Gryaznov, V.M.; Sarylova, M.E. Palladium-based Alloy. US Patent 4,489,039, Dec. 18, 1984.
209. Lewis, F.A. Hydrogen interstitial structures in palladium–silver membranes. Platinum Met. Rev. **1993**, *37* (4), 220.
210. Gryaznov, V.M.; Mishchenko, A.P.; Polyakova, V.P.; Roshan, N.R.; Savitskii, E.M.; Smirnov, V.S.; Khrapova, E.V.; Shimulis, V.I. Palladium–ruthenium alloys as membrane catalysts. Dokl. Akad. Nauk SSSR **1973**, *211* (3), 604.
211. Cabrera, A.L.; Morales L.E.; Hasen, J.; Schuller, I.K. Structural changes induced by hydrogen absorption in palladium and palladium–ruthenium alloys. Appl. Phys. Lett. **1995**, *66* (10), 1216.
212. Cabrera, A.L.; Morales-Leal, E.; Hasen, J.; Schuller, I.K. Changes in crystallographic orientation of thin foils of palladium and palladium alloys after the absorption of hydrogen. Catal. Lett. **1995**, *30*, 11.
213. Darling, A.S. Trennung und Reinigung von Wasserstoff durch Permeation an Membranen aus Palladium–Legierungen. Chem.-Ing. -Tech. **1965**, *37* (1), 18.

214. Musket, R.G. Effects of contamination on the interactions of hydrogen gas with palladium: A review. J. Less-Common Met. **1976**, *45*, 173.

215. Kompaniets, T.N.; Kurdyumov, A.A. Surface processes in hydrogen permeation through metal membranes. Prog. Surf. Sci. **1984**, *17*, 75.

216. Shiraishi, T.; Nishikawa, M.; Fukumatsu, T. Permeation of multicomponent hydrogen isotopes through nickel. J. Nucl. Mater. **1998**, *254*, 205.

217. Balovnev, Y.A. Diffusion of hydrogen in palladium. Russ. J. Phys. Chem. **1974**, *48*, 409.

218. Pugachev, V.A.; Busol, F.I.; Nikolaev, E.I.; Nam, B.P. Penetration and diffusion of hydrogen in palladium–silver alloys. Russ. J. Phys. Chem. **1975**, *49*, 1045.

219. Doyle, M.L.; Harris, I.R. Order-disorder transformations and hydrogen solubility in a series of Pd–Y solid solution alloys. Z. Phys. Chem. N.F. **1989**, *163*, 59.

220. Axelrod, S.D.; Makrides, A.C. X-ray studies of hydrogen–silver–palladium electrodes. J. Phys. Chem. **1964**, *68* (8), 2154.

221. Makrides, A.C. Absorption of hydrogen by silver–palladium alloys. J. Phys. Chem. **1964**, *68* (8), 2160.

222. Oates, W.A.; Flanagan, T.B. The solubility of hydrogen in transition metals and their alloys. Prog. Solid State Chem. **1981**, *13*, 193.

223. Latyshev, V.V.; Gur'yanov, V.G.; Asliddinova, M.Y.; Cholovyan, I.I.; Mironova, G.I. Permeation of impurities through hydrogen diffusion membranes of palladium alloys. Phys. Met. Metallogr. **1991**, *71* (2), 202.

224. Latyshev, V.V.; Gur'yanov, V.G.; Asliddinova, M.Y.; Cholovyan, I.I.; Mironova, G.I. Hydrogen-stimulated penetration of impurities through palladium alloy membranes. Russ. J. Phys. Chem. **1991**, *65* (5), 755.

225. Latyshev, V.V.; Gur'yanov, V.G.; Asliddinova, M.Y.; Cholovyan, I.I.; Mironova, G.I. Hydrogen-stimulated impurity diffusion through palladium–alloy membranes. Sov. Phys. Tech. Phys. (Zh. Tekh. Fiz.) **1991**, *36* (9), 1058.

226. Doroshin, A.Y.; Livshits, A.I.; Samartsev, A.A. The effect of carbon coverage on the interaction of hydrogen atoms and molecules with a palladium surface and on palladium membrane permeation by hydrogen. Sov. J. Chem. Phys. (Khim. Fiz.) **1987**, *4* (8), 1824.

227. Moss, T.S.; Peachey, N.M.; Snow, R.C.; Dye, R.C. Multilayer metal membranes for hydrogen separation. Int. J. Hydrogen Energy **1998**, *23* (2), 99.

228. Zheng, G.; Popov, B.N.; White, R.E. Hydrogen-atom direct-entry mechanism into metal membranes. J. Electrochem. Soc. **1995**, *142* (1), 154.

229. Flanagan, T.B.; Oates, W.A. The palladium–hydrogen system. Annu. Rev. Mater. Sci. **1991**, *21*, 269.
230. Krykin, M.A.; Timashev, S.F. ''Nonequilibrium'' effects in gas transport across solid-state membranes. Sov. Phys. Solid State (Fiz. Tverd. Tela) **1985**, *27* (9), 1529.
231. Stoneham, A.M. Theory of the diffusion of hydrogen in metals. Ber. Bunsen-Ges. **1972**, *76* (8), 816.
232. Flanagan, T.B.; Oates, W.A. Thermodynamics of metal/hydrogen systems. Ber. Bunsen-Ges. **1972**, *76* (8), 706.
233. Castellan, G.W. The transmission of electrolytically deposited hydrogen through a palladium membrane electrode. I. The rate equations. J. Electrochem. Soc. **1964**, *111* (11), 1273.
234. Tovbin, Y.K. Molecular-kinetic models of the transfer of substances in inorganic membranes. Russ. Chem. Rev. (Usp. Khim.) **1988**, *57* (6), 520.
235. Kandasamy, K.; Lewis, F.A. Important Gorsky effect influences on diffusion coefficients in metal–hydrogen systems. Int. J. Hydrogen Energy **1999**, *24*, 763.
236. Uchida, H. Surface processes of $H_2$ on rare earth based hydrogen storage alloys with various surface modifications. Int. J. Hydrogen Energy **1999**, *24*, 861.
237. Fast, J.D. Experiments on the permeation of gases through metal walls. Philips Tech. Rev. **1942**, *7* (3), 74.
238. Ward, T.L.; Dao, T. Model of hydrogen permeation behavior in palladium membranes. J. Membr. Sci. **1999**, *153*, 211.
239. Andrew, P.L.; Haasz, A.A. Models for hydrogen permeation in metals. J. Appl. Phys. **1992**, *72* (7), 2749.
240. Zaika, Y.V.; Gabis, I.E. Determination of the parameters of hydrogen permeability of metals by the method of adjoint equations. Ind. Lab. (Zavod. Lab.) **1996**, *62* (1), 16.
241. Ali-Khan, I.; Dietz, K.J.; Waelbroeck, F.G.; Wienhold, P. The rate of hydrogen release out of clean metallic surfaces. J. Nucl. Mater. **1978**, *76 & 77*, 337.
242. Al-Shammary, A.F.Y.; Caga, I.T.; Winterbottom, J.M.; Tata, A.Y.; Harris, I.R. Palladium-based diffusion membranes as catalysts in ethylene hydrogenation. J. Chem. Technol. Biotechnol. **1991**, *52*, 571.
243. Kolesnichenko, I.I.; Michri, A.A.; Pshenichnikov, A.G. Kinetics of hydrogen transport through palladium membranes under conditions of the electrochemical injection and extraction of hydrogen. Sov. Electrochem. (Elektrokhimiya) **1989**, *25* (12), 1501.
244. Samartsev, A.A. Penetration of hydrogen through metal membranes in low-pressure region. Kinet. Catal. **1985**, *26* (4), 703.

245. Buevich, Y.A.; Ivonin, A.K. Diffusion-kinetic theory of the gas permeability of membranes. Russ. J. Phys. Chem. **1987**, *61* (10), 1482.
246. Namba, T.; Yamawaki, M.; Kanno, M. Surface effects on hydrogen permeation through fusion reactor materials: A new model and its application to vanadium membrane. J. Fac. Eng. Univ. Tokyo, Ser. B **1984**, *37* (3), 491.
247. Auer, W.; Grabke, H.J. The kinetics of hydrogen absorption in palladium (α- and β-phase) and palladium–silver–alloys. Ber. Bunsenges. **1974**, *78* (1), 58.
248. Swansiger, W.A.; Swisher, J.H.; Darginis, J.P.; Schoenfelder, C.W. Hydrogen permeation in palladium–chromium alloys. J. Phys. Chem. **1976**, *80* (3), 308.
249. Altunoglu, A.K.; Blackburn, D.A.; Braithwaite, N.S.J. Permeation of hydrogen through nickel foils: Surface reaction rates at low temperatures. J. Less-Common Met. **1991**, *172–174*, 718.
250. Fujita, H.; Okada, S.; Fujita, F.; Sakamoto, H.; Higashi, K.; Hyodo, T. Ratio of permeabilities of tritium to protium through palladium–alloy membrane. J. Nucl. Sci. Technol. **1980**, *17* (6), 436.
251. Kizu, K.; Pisarev, A.; Tanabe, T. Co-permeation of deuterium and hydrogen through Pd. J. Nucl. Mater. **2001**, *289* (3), 291.
252. Lewis, F.A. Solubility of hydrogen in metals. Pure Appl. Chem. **1990**, *62* (11), 2091.
253. Bruzzoni, P.; Carranza, R.M.; Collet Lacoste, J.R. Influence of palladium films on hydrogen gas entry into iron: A study by electrochemical impedance spectroscopy. Int. J. Hydrogen Energy **2000**, *25* (1), 61.
254. Bucur, R.V. Effect of trapping on the solubility and diffusivity of hydrogen in palladium (α-phase). J. Mater. Sci. **1987**, *22*, 3402.
255. Archer, M.D.; Grant, N.C. Achievable boundary conditions in potentiostatic and galvanostatic hydrogen permeation through palladium and nickel foils. Proc. R. Soc. London, Ser. A **1984**, *395* (1808), 165.
256. Hickman, R.G. Diffusion and permeation of deuterium in palladium–silver at high temperature and pressure. J. Less-Common Met. **1969**, *19* (4), 369.
257. Sieverts, A.; Krumbhaar, W. Über die Löslichkeit von Gasen in Metallen und Legierungen. Ber. Dtsch. Chem. Ges. **1910**, *43*, 893.
258. Manchester, F.D.; San-Martin, A.; Pitre, J.M. H–Pd (Hydrogen–Palladium). In *Phase Diagrams of Binary Hydrogen Alloys*; Manchester, F.D., Ed.; ASM International: Materials Park, Ohio, US, 2000; 158.
259. Hurlbert, R.C.; Konecny, J.O. Diffusion of hydrogen through palladium. J. Chem. Phys. **1961**, *34* (2), 655.
260. Evans, M.J.B. Surface area effects on the sorption of hydrogen by palladium. Can. J. Chem. **1974**, *52*, 1200.

261. Lacher, J.R. A theoretical formula for the solubility of hydrogen in palladium. Proc. R. Soc. London, Ser. A **1937**, *161*, 525.
262. Kizu, K.; Tanabe, T. Deuterium permeation through metals under hydrogen counter flow. J. Nucl. Mater. **1999**, *266–269*, 561.
263. Andrew, P.L.; Haasz, A.A. Hydrogen permeation through copper-coated palladium. J. Appl. Phys. **1991**, *70* (7), 3600.
264. Kizu, K.; Tanabe, T. Counter-diffusion and counter-permeation of deuterium and hydrogen through palladium. J. Nucl. Mater. **1998**, *258–263*, 1133.
265. Zubarev, Y.A.; Mikhalenko, I.I.; Yagodovskii, V.D. Chemisorption of hydrogen on palladium foil and films. Kinet. Catal. **1983**, *24*, 1017.
266. Fort, D.; Harris, I.R. The physical properties of some palladium alloy hydrogen diffusion membrane materials. J. Less-Common Met. **1975**, *41*, 313.
267. Goto, S.; Assabumrungrat, S.; Tagawa, T.; Praserthdam, P. The effect of direction of hydrogen permeation on the rate through a composite palladium membrane. J. Membr. Sci. **2000**, *175*, 19.
268. Deckman, H.W.; Corcoran, E.W.; McHenry, J.A.; Meldon, J.H.; Papavassiliou, V.A. Pressure drop membrane reactor equilibrium analysis. Catal. Today **1995**, *235* (3–4), 357.
269. Goto, S.; Assabumrungrat, S.; Tagawa, T.; Praserthdam, P. Dependence of hydrogen pressure on the permeation rate through composite palladium membranes. J. Chem. Eng. Jpn. **2000**, *33* (2), 330.
270. Huang, T.-C.; Wei, M.-C.; Chen, H.-I. Permeation of hydrogen through palladium/alumina composite membranes. Sep. Sci. Technol. **2001**, *36* (2), 199.
271. Dittmeyer, R.; Hollein, V.; Quicker, P.; Emig, P.; Hausinger, G.; Schmidt, F. Factors controlling the performance of catalytic dehydrogenation of ethylbenzene in palladium composite membrane reactors. Chem. Eng. Sci. **1999**, *54* (10), 1431.
272. Itoh, N.; Wu, T.-H.; Haraya, K. Two- and three-dimensional analysis of diffusion through a dense membrane supported on a porous material. J. Membr. Sci. **1995**, *99*, 175.
273. Collins, J.P.; Way, J.D. Preparation and characterization of a composite palladium–ceramic membrane. Ind. Eng. Chem. Res. **1993**, *32* (12), 3006.
274. Itoh, N.; Xu, W.-C.; Haraya, K. Radial mixing diffusion of hydrogen in a packed-bed type of palladium membrane reactor. Ind. Eng. Chem. Res. **1994**, *33*, 197.
275. Hara, S.; Sakaki, K.; Itoh, N. Decline in hydrogen permeation due to concentration polarization and CO hindrance in a palladium membrane reactor. Ind. Eng. Chem. Res. **1999**, *38*, 4913.

276. Jayaraman, V.; Lin, Y.S. Synthesis and hydrogen permeation properties of ultrathin palladium–silver alloy membranes. J. Membr. Sci. **1995**, *104*, 251.
277. Ash, R.; Barrer, R.M. Permeation of hydrogen through metals. Philos. Mag. **1959**, *4*, 1197.
278. Li, A.; Liang, W.; Hughes, R. Fabrication of defect-free Pd/$\alpha-Al_2O_3$ composite membranes for hydrogen separation. Thin Solid Films **1999**, *350*, 106.
279. Vandyshev, A.B.; Makarov, V.M.; Murav'ev, L.L.; Tabachnik, E.B.; Nikishin, S.N. Modeling of high-temperature membrane apparatuses for the production of ultrapure hydrogen. Theor. Found. Chem. Eng. (Teor. Osn. Khim. Tekhnol.) **1996**, *30* (5), 506.
280. Murav'ev, L.L.; Vandyshev, A.B.; Makarov, V.M. The modeling of membrane extraction of hydrogen from multicomponent gas mixtures. Theor. Found. Chem. Eng. (Teor. Osn. Khim. Tekhnol.) **1999**, *33* (2), 169.
281. Vandyshev, A.B.; Murav'ev, L.L.; Makarov, V.M.; Usova, T.B. Modeling of the membrane extraction of extra-pure hydrogen from chemically noninteracting multicomponent gaseous mixtures. Chem. Pet. Eng. (Khim. Neftegazov. Mashinostr.) **1999**, *35* (1–2), 3.
282. Penzhorn, R.-D.; Berndt, U.; Kirste, E.; Chabot, J. Performance tests of palladium/silver permeators with tritium at the tritium laboratory Karlsruhe. Fusion Technol. **1997**, *32*, 232.
283. Baboshin, V.M.; Buevich, J.A.; Ivonin, A.K.; Kirnos, I.V.; Kukui, B.G. Diffusion separation of hydrogen from gas mixtures. Russ. J. Eng. Phys. (Inzh.-Fiz. Zh.) **1984**, *47* (1), 821.
284. Belyakov, Y.I.; Zvezdin, Y.I.; Kurakin, V.A. Effect of mechanical surface treatment on the permeability to hydrogen of metallic membranes. Russ. J. Phys. Chem. **1980**, *54* (11), 1603.
285. Pyun, S.-I.; Lim, C.; Kim, K.-B. An investigation of the electrochemical kinetics of deuterium insertion into a Pd membrane electrode in 0.1 LiOD solution by the a.c. impedance technique. J. Alloys Compd. **1994**, *203*, 149.
286. Bucur, R.V. The influence of experimental conditions upon the measurements of hydrogen diffusion in palladium by electrochemical permeation methods. Z. Phys. Chem. N.F. **1985**, *146*, 613.
287. Pu, C.; Huang, W.; Ley, K.L.; Smotkin, E.S. A methanol impermeable proton conducting composite electrolyte system. J. Electrochem. Soc. **1995**, *142* (7), L119.
288. Cabot, P.L.; Guezala, E.; Calpe, J.C.; García, M.T.; Casado, J. Application of Pd-based electrodes as hydrogen diffusion anodes in alkaline fuel cells. J. Electrochem. Soc. **2000**, *147* (1), 43.

289. Lewis, F.A.; Sakamoto, Y.; Tong, X.Q. Strain gradient effects on hydrogen permeation through hydrided metals. Int. J. Hydrogen Energy **1995**, *20* (5), 365.
290. Edlund, D. Hydrogen-Permeable Metal Membrane and Method for Producing the Same. US Patent 6,152,995, Nov 28, 2000.
291. Juda, W.; Krueger, C.W.; Bombard, R.T. Method of Fabricating Thinned Free-Standing Metallic Hydrogen-selective Palladium-bearing Membranes and Novel Pin-hole-Free Membranes Formed Thereby. US Patent 6,103,028, Aug. 15, 2000.
292. Mishchenko, A.P.; Gryaznov, V.M.; Sarylova, M.E. Effect of thermodiffusion and chemical treatment of the surface of membrane catalysts made from palladium alloys with ruthenium and rhodium on penta-1,3-diene hydrogenation. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1991**, *40* (6 (1)), 1154.
293. Mishchenko, A.P.; Sarylova, M.E.; Litvinov, I.A.; Bezruk, L.I.; Gryaznov, V.M. Influence of heat-treating conditions on formation of pore structure of surface layer of palladium–ruthenium alloy foil. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1985**, *34* (3 (1)), 524.
294. Sarylova, M.E.; Mishchenko, A.P.; Gryaznov, V.M.; Litvinov, A. Effect of preparative conditions of a porous surface layer on the hydrogen permeability of palladium/ruthenium alloy membranes. Bull. Acad. Sci. USSR (Iz. Akad. Nauk SSSR, Ser. Khim.) **1991**, *40* (6), 1149.
295. Mishchenko, A.P.; Gryaznov, V.M.; Sarylova, M.E. Influence of thermodiffusive and chemical treatment of membrane catalyst surfaces formed from alloys of palladium with rhodium or ruthenium on hydrogeation of 1,3-pentadiene. Chem. Abstr. **1991**, *115*, 255409a.
296. Khrushcheva, E.I.; Tarasevich, M.R. Electrochemical determination of surface area of metals. Russ. Chem. Rev. **1978**, *47* (5), 416.
297. Baranov, Y.M.; Zozulya, V.Y.; Nazarkina, E.B. Transport of hydrogen across thin films of palladium alloys. Sov. Chem. Ind. (Khim. Prom-st.) **1989**, *21* (1), 100.
298. Nishikawa, M.; Shiraishi, T.; Kawamura, Y.; Takeishi, T. Permeation rate of hydrogen isotopes through palladium–silver alloy. J. Nucl. Sci. Technol. **1996**, *33* (10), 774.
299. Doyle, B.L. A simple theory for maximum H inventory and release: A new transport parameter. J. Nucl. Mater. **1982**, *111 & 112*, 628.
300. Liu, S.-Y.; Kao, Y.-H.; Su, O.Y.; Perng, T.-P. In situ monitoring of hydrogen absorption-desorption in Pd and $Pd_{77}Ag_{23}$ films by an electrochemical quartz crystal microbalance. J. Alloys Compd. **1999**, *293–295*, 468.
301. Tontegode, A.Y. Reduction in hydrogen permeability of palladium foils

with carbon films. Sov. Tech. Phys. Lett. (Pis'ma Zh. Tekh. Fiz.) **1977**, *3* (7), 260.

302. Criscuoli, A.; Basile, A.; Drioli, E.; Loiacono, O. An economic feasibility study for water gas shift membrane reactor. J. Membr. Sci. **2001**, *181*, 21.
303. Richardson, O.W.; Nicol, J.; Parnell, T. The diffusion of hydrogen through hot platinum. Philos. Mag. **1904**, *8* (43), 1.
304. Mardilovich, P.P.; She, Y.; Ma, Y.H.; Rei, M.-H. Defect-free palladium membranes on porous stainless-steel support. AIChE J. **1998**, *44* (2), 310.
305. Fort, D.; Farr, J.P.G.; Harris, I.R. A comparison of palladium–silver and palladium–yttrium alloys as hydrogen separation membranes. J. Less-Common Met. **1975**, *39* (2), 293.
306. van Swaay, M.; Birchenall, C.E. Permeability and diffusion of hydrogen through palladium. AIME Trans. **1960**, *218* (4), 285.
307. Rodina, A.A.; Doronicheva, N.I. Rate of diffusion of hydrogen through palladium. Russ. J. Phys. Chem. **1966**, *40* (7), 788.
308. Le Claire, A.D. Permeation of gases through solids. Diffus. Defect Data **1983**, *33*, 1.
309. Peachey, N.M.; Snow, R.C.; Dye, R.C. Composite Pd/Ta metal membranes for hydrogen separation. J. Membr. Sci. **1996**, *111*, 123.
310. Altonoglu, A.K.; Braithwaite, N.S.J. The science and application of modulated permeation experiments. J. Alloys Compd. **1995**, *231*, 302.
311. Antoniazzi, A.B.; Haasz, A.A.; Stangeby, P.C. The effect of adsorbed carbon and sulphur on hydrogen permeation through palladium. J. Nucl. Mater. **1989**, *162–164*, 1065.
312. Steward, S.A. Review of Hydrogen Isotope Permeability Through Materials. In *US National Laboratory Report*; 1983; UCRL-53441.
313. Weirich, W.; Biallas, B.; Kügler, B.; Oertel, M.; Pietsch, M.; Winkelmann, U. Development of a laboratory cycle for a thermochemical water-splitting process (Me/MeH cycle). Int. J. Hydrogen Energy **1986**, *11* (7), 459.
314. Uchida, H.; Fromm, E. Effect of palladium and oxygen layers on the hydrogen absorption rate of tantalum films at 300 K. J. Less-Common Met. **1983**, *95*, 153.
315. Uchida, H.; Fromm, E. Kinetics of hydrogen absorption by titanium, tantalum, tungsten, iron, and palladium films with and without oxygen preabsorption at 300 K. J. Less-Common Met. **1983**, *95*, 139.
316. Uchida, H.H.; Wulz, H.-G.; Fromm, E. Catalytic effect of nickel, iron and palladium on hydriding titanium and storage materials. J. Less-Common Met. **1991**, *172–174*, 1076.
317. Ashida, K.; Watanabe, K.; Ikeno, S.; Mori, K. Surface modification of Zr-based alloys applicable for tritium processing. Fusion Eng. Des. **1998**, *39–40*, 1049.

318. Andrew, P.L.; Haasz, A.A. Effect of thin copper and palladium films on hydrogen permeation through iron. J. Less-Common Met. **1991**, *172–174*, 732.
319. Ashida, K.; Nishida, W.; Nagata, J.-I.; Nishimura, Y.; Watanabe, K. Recovery of deuterium from argon carrier gas by ZrNi modified with electroless Pd coating. Mater. Trans. JIM **1999**, *40* (9), 851.
320. Libowitz, G.G.; Maeland, A.J. Hydride formation by b.c.c. solid solution alloys. Mater. Sci. Forum **1988**, *31*, 177.
321. Hill, E.F. Method for Removing Hydrogen from Liquid Alkali Metals and the Like. US Patent 3,622,303, Aug. 28, 1971.
322. Holleck, G.L. Hydrogen Diffusion through (palladium–silver)–tantalum–(palladium–silver) composites. J. Phys. Chem. **1970**, *74* (9), 1957.
323. Nakamura, K.; Uchida, H.; Fromm, E. Kinetics of hydrogen absorption of tantalum coated with thin films of palladium, iron, nickel, copper and silver. J. Less-Common Met. **1981**, *80*, P19.
324. Šušić, M.V.; Ribnikar, S.V. Absorption of hydrogen by palladium-coated tantalum powder. Int. J. Hydrogen Energy **1994**, *19* (9), 751.
325. Lagos, M.; Martinez, G.; Schuller, I.K. Kinetics of hydrogen absorption in transition metals and subsurface bonding. Phys. Rev. B **1984**, *29* (10), 5979.
326. Strongin, M.; El-Batanouny, M.; Pick, M.A. Structure of Pd overlayers on Nb and Ta and the relationship to hydrogen uptake. Phys. Rev. B **1980**, *22* (6), 3126.
327. Züchner, H.; Schluter, H.-J.; Rauf, T.; Hergemoller, R. Properties of thin palladium-films and their hydrogen-permeability. Ber. Bunsen-Ges. **1991**, *95* (11), 1401.
328. Züchner, H. Multilayer problems in studying the diffusion of hydrogen in metals by time-lag techniques. Trans. JIM (Proceedings of JIMIS—2. Hydrogen in Metals) **1980**, *21* (Supplement), 101.
329. Makrides, A.C.; Wright, M.A.; Jewett, D.N. Separation of hydrogen by permeation. US Patent 3,350,846, Nov. 7, 1967.
330. El-Batanouny, M.; Strongin, M.; Williams, G.P. Relationship between electronic structure and hydrogen-uptake kinetics. Am. Phys. Soc. **1981**, *46* (4), 269.
331. Davenport, J.W.; Dienes, G.J.; Johnson, R.A. Surface effects on the kinetics of hydrogen absorption by metals. Phys. Rev. B **1982**, *25* (4), 2165.
332. Buxbaum, R.E.; Subramanian, R.; Park, J.H.; Smith, D.L. Hydrogen transport and embrittlement for palladium coated vanadium–chromium–titanium alloys. J. Nucl. Mater. **1996**, *233–237*, 510.
333. Buxbaum, R.E. The use of zirconium–palladium windows for the

separation of tritium from the liquid metal breeder-blanket of a fusion reactor. Sep. Sci. Technol. **1983**, *18* (12 & 13), 1251.

334. Amano, M.; Komaki, M.; Nishimura, C. Hydrogen permeation characteristic of palladium-plated V–Ni alloy membranes. J. Less-Common Met. **1991**, *172–174*, 727.
335. Pick, M.A.; Davenport, J.W.; Strongin, M.; Dienes, G.J. Enhancement of hydrogen uptake rates for Nb and Ta by thin surface overlayers. Phys. Rev. Lett. **1979**, *43* (4), 286.
336. Züchner, H.; Boes, N. SIMS—Untersuchungen zum Einfluβ von Oberflächenschichten auf die Wasserstoffdurchlässigkeit von Tantal–Folien. Z. Phys. Chem. N.F. **1974**, *93*, 65.
337. Boes, N.; Züchner, H. Diffusion of hydrogen and deuterium in Ta, Nb, and V. Phys. Status Solidi A **1973**, *17*, K111.
338. Boes, N.; Züchner, H. Secondary ion mass spectrometry and Auger electron spectroscopy investigations of Vb metal foils prepared for hydrogen permeation measurements. Surf. Technol. **1978**, *7*, 401.
339. Moss, T.S.; Dye, R.C. *Engineering Materials for Hydrogen Separation, DE97002456*; Los Alamos National Laboratory: Los Alamos, New Mexico, US, 1996.
340. Moss, T.S.; Dye, R.C. *Composite Metal Membranes for Hydrogen Separation Applications, DE97007586*; Los Alamos National Laboratory: Los Alamos, New Mexico, US, 1997.
341. Peachey, N.M.; Dye, R.C. *High Temperature Efforts at Los Alamos National Laboratory, DE96011306*; Los Alamos National Laboratory: Los Alamos, New Mexico, US, 1995.
342. Peachey, N.M.; Dye, R.C.; Snow, R.C.; Birdsell, S.A. Composite Metal Membrane. US Patent 5,738,708, Apr. 14, 1998.
343. Cussler, E.L. *Diffusion: Mass Transfer in Fluid Systems,* 2nd Ed.; Cambridge University Press: New York, 1997.
344. Mulder, M. *Basic Principles of Membrane Technology*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.
345. Chai, M.; Machida, M.; Eguchi, K.; Arai, H. Gas permeation through microporous alumina membranes containing highly dispersed metal particles. Chem. Lett. **1992** (6), 979.
346. Higashi, K.; Ito, H.; Oishi, J. Surface diffusion phenomena in gaseous diffusion, (II). J. Nucl. Sci. Technol. **1964**, *1* (8), 298.
347. Eickmann, U.; Werner, U. Gas separation using porous membrane. Ger. Chem. Eng. **1985**, *8*, 186.
348. Nam, S.-E.; Lee, K.-H. A study on the palladium–nickel composite membrane by vacuum electrodeposition. J. Membr. Sci. **2000**, *170* (1), 91.
349. Shu, J.; Grandjean, B.P.A.; Kaliaguine, S.; Ciaveralla, P.; Giroir-Fendler,

A.; Dalmon, J.-A. Hysteresis in hydrogen permeation through palladium membranes. J. Chem. Soc., Faraday Trans. **1996**, *92* (15), 2745.

350. Votyakov, E.V.; Vasyutkin, N.F.; Senyavin, M.M.; Tovbin, Y.K. Interrelation between the phase state of palladium membranes and the characteristics of hydrogen transfer. Russ. J. Phys. Chem. **1999**, *73* (12), 1924.
351. Livshits, A.I.; Samartsev, A.A. Attaining the extreme values of the adhesion and penetration probabilities in the system of hydrogen and a palladium membrane. Sov. Phys. Tech. Phys. (Zh. Tekh. Fiz.) **1979**, *49* (11), 1365.
352. Li, A.; Hughes, R. The effect of carbon monoxide and steam on the hydrogen permeability of a Pd/stainless steel membrane. J. Membr. Sci. **2000**, *165*, 135.
353. Bukalov, A.P.; Koshel', V.I. Temperature relationship of concentration dilatation and specific capacity of hydrogen diffusion filters of V-1 alloy. Sov. Mater. Sci. (Fiz.-Khim. Mekh. Mater.) **1985**, *21* (1), 99.
354. Khrisanfova, L.V.; Zaidenman, I.A.; Rodina, A.A. Asymmetric diffusion of hydrogen through bimetallic membranes. Russ. J. Phys. Chem. **1975**, *49* (4), 561.
355. Herzog, F.; Glaubitz, D. Production of hydrogen from the Na/NaH-process. Int. J. Hydrogen Energy **1990**, *15* (1), 13.
356. Pick, M.A.; Sonnenberg, K. A model for atomic hydrogen-metal interactions-application to recycling, recombination and permeation. J. Nucl. Mater. **1985**, *131*, 208.
357. Lee, W.-J.; Pyun, S.-I.; Yang, T.-H.; Kim, J.-D.; Baek, Y.-H.; Kim, H.-G. Hydrogen transport through Pd–Ni alloy electrodeposited on Pd substrate. J. Solid State Electrochem. **1997**, *1*, 120.
358. Kompaniets, T.N.; Kurakin, V.A.; Kurdyumov, A.A.; Lyasnikov, V.N. Investigation of the kinetics of permeation of hydrogen through copper membranes. Sov. Phys. Solid State (Fiz. Tverd. Tela) **1978**, *20* (12), 2043.
359. Glazunov, G.P. Hydrogen permeation through palladium after hydrogen-thermal treatment and exposure to a plasma of glow discharge in hydrogen, helium and argon. Int. J. Hydrogen Energy **1997**, *22* (2/3), 263.
360. Basile, A.; Paturzo, L.; Laganà, F. The partial oxidation of methane to syngas in a palladium membrane reactor: Simulation and experimental studies. Catal. Today **2001**, *67*, 65.
361. Worsham, J.E.; Wilkinson, M.K.; Shull, C.G. Neutron-diffraction observations on the palladium–hydrogen and palladium–deuterium systems. J. Phys. Chem. Solids **1957**, *3*, 303.
362. Maeda, T.; Naito, S.; Yamamoto, M.; Mabuchi, M.; Hashino, T. High-

temperature diffusion of hydrogen and deuterium in palladium. J. Chem. Soc., Faraday Trans. **1994**, *90* (6), 899.

363. Kang, B.-S.; Sohn, K.-S. Diffusion processes and interactions of hydrogen atoms in Pd. Physica B **1995**, *205*, 163.
364. Katsnel'son, A.A.; Knyazeva, M.A.; Revkevich, G.P.; Olemskoı, A.I. Characteristics of the evolution of defect structure during phase transformations in the Pd–H system. Phys. Solid State (Fiz. Tverd. Tela) **1997**, *39* (7), 1132.
365. Ponyatovskii, E.G.; Antonov, V.E.; Belash, I.T. Properties of high pressure phases in metal–hydrogen systems. Sov. Phys. Usp. (Usp. Fiz. Nauk) **1982**, *25* (8), 596.
366. Tsuchida, T. Role of hydrogen atoms in palladium. J. Phys. Soc. Jpn. **1963**, *18* (7), 1016.
367. Bohmholdt, G.; Wicke, E. Zur Diffusion von Wasserstoff und Deuterium in Palladium und Pd–Legierungen. Z. Phys. Chem. N.F. **1967**, *56*, 133.
368. Davis, P.P.; Seymour, E.F.W.; Zamir, D.; Williams, W.D.; Cotts, R.M. Nuclear magnetic resonance study of hydrogen diffusion in palladium–silver alloys. J. Less-Common Met. **1976**, *49*, 159.
369. Vykhodets, V.B.; Demin, V.B.; Geld, P.V. Hydrogen Isotope diffusivity and solubility in nickel, palladium, and copper. Phys. Status Solidi A **1976**, *34*, 787.
370. Sköld, K.; Nelin, G. Diffusion of hydrogen in the α-phase of Pd–H studied by small energy transfer neutron scattering. J. Phys. Chem. Solids **1967**, *28*, 2369.
371. Smirnov, L.I. Diffusion of hydrogen in metals at arbitrary concentration gradients. Int. J. Hydrogen Energy **1999**, *24*, 813.
372. Feldberg, S.W.; Reilly, J.J. Phenomenological treatment of hydrogen transport in a metal/metal hydride system. J. Electrochem. Soc. **1997**, *144* (12), 4260.
373. Smirnov, L.I.; Filonenko, S.S. Concerning the concentration dependence of the diffusion coefficient of hydrogen in aluminium. Phys. Met. Metallogr. **1989**, *67* (2), 25.
374. Smirnov, L.I.; Gol'tsov, V.A. Dynamics of metal–hydrogen systems in a continuum approximation and some hydrogen-induced elastic effects. Phys. Met. Metallogr. **1997**, *84* (6), 599.
375. Smirnov, L.I.; Gol'tsov, V.A. Nonlinear and crossover effects in the diffusion penetration of hydrogen through a metallic membrane. Russ. J. Eng. Phys. (Inzh.-Fiz. Zh.) **1988**, *55* (3), 981.
376. Smirnov, L.I. Effect of the concentration dependence of the diffusion coefficient on the distribution and flow of hydrogen in palladium membranes. Russ. J. Eng. Phys. (Inzh.-Fiz. Zh.) **1990**, *59* (10), 1280.

377. Jemaa, N.; Grandjean, B.P.A.; Kaliaguine, S. Diffusion coefficient of hydrogen in a Pd–Ag membrane: Effect of hydrogen solubility. Can. J. Chem. Eng. **1995**, *73*, 405.
378. Lewis, F.A.; Kandasamy, K.; Baranowski, B. The ‘‘uphill’’ diffusion of hydrogen. Platinum Met. Rev. **1988**, *32* (1), 22.
379. Zoltowski, P. Effects of self-induced mechanical stress in hydrogen sorption by metals, by EIS. Electrochim. Acta **1999**, *44*, 4415.
380. Tong, X.Q.; McNicholl, R.-A.; Kandasamy, K.; Lewis, F.A. Hydrogen permeation in stressed and strained membranes of palladium alloys. Int. J. Hydrogen Energy **1992**, *17* (10), 777.
381. Tong, X.Q.; Sakamato, Y.; Lewis, F.A.; Bucur, R.V.; Kandasamy, K. ‘‘Uphill’’ hydrogen diffusion effects and hydrogen diffusion coefficients in palladium. Int. J. Hydrogen Energy **1997**, *22* (2/3), 141.
382. Tong, X.Q.; Bucur, R.V.; Kandasamy, K.; Lewis, F.A. Strain gradient related uphill hydrogen diffusion phenomena in $Pd_{77}Ag_{23}H_n$. Z. Phys. Chem. N.F. **1993**, *181*, 225.
383. Tong, X.Q.; Kandasamy, K.; Lewis, F.A. Influences of lattice strain gradients on hydrogen permeation through palladium membranes containing hydrogen contents in $\alpha$, $\alpha+\beta$ and $\beta$ phase concentration ranges. Scr. Metall. **1990**, *24* (10), 1923.
384. Sakamoto, Y.; Tanaka, H.; Lewis, F.A.; Tong, X.Q.; Kandasamy, K. ‘‘Uphill’’ hydrogen diffusion effects of hydrogen interstitial strain gradients in palladium and palladium alloys. Int. J. Hydrogen Energy **1996**, *21* (11/12), 1025.
385. Sakamoto, Y.; Tanaka, H.; Lewis, F.A.; Tong, X.Q. Observations of ‘‘uphill’’ diffusion of hydroegn in palladium and nickel membranes by an electrochemical permeation method. Z. Phys. Chem. N.F. **1993**, *181*, 219.
386. Sakamoto, Y.; Tanaka, H.; Sakamoto, F.; Lewis, F.A.; Tong, X.Q. Self strain gradient induced diffusion of hydrogen in Pd–Ag alloy membranes. Int. J. Hydrogen Energy **1995**, *20* (1), 35.
387. Sakamoto, Y.; Tong, X.Q.; Lewis, F.A. Effects of non-Fickian uphill components of permeation flux on estimations of hydrogen diffusion coefficients in the Pd/H system. Scr. Metall. **1991**, *25*, 1629.
388. Yang, T.-H.; Pyun, S.-I.; Yoon, Y.-G. Hydrogen transport through Pd electrode current transient analysis. Electrochim. Acta **1997**, *42* (11), 1701.
389. Tong, X.Q.; Lewis, F.A. Indications of linearity deviations of steady-state concentration profiles in hydrogen permeation membranes. Int. J. Hydrogen Energy **1995**, *20* (8), 641.
390. Lewis, F.A.; Tong, X.Q.; Bucur, R.V. Permeation of hydrogen through palladium–silver membranes. Platinum Met. Rev. **1991**, *35* (3), 138.

391. Lewis, F.A.; Tong, X.Q.; Kandasamy, K. Lattice strain gradient influences on steady-state rates of hydrogen permeation through membranes. Int. J. Hydrogen Energy **1993**, *18* (6), 481.
392. Sakamoto, Y.; Tanaka, H.; Lewis, F.A.; Tong, X.Q. Strain gradient-induced diffusion of hydrogen in palladium and nickel membranes. Int. J. Hydrogen Energy **1992**, *17* (12), 965.
393. Mällo, A.; Krozer, A. ''Up-hill'' diffusion and hydrogen–hydrogen interaction in palladium–platinum alloys. J. Less-Common Met. **1991**, *167*, 305.
394. Simon, A.M. A criticism of the postulated quadratic steady-state concentration profile for strain gradient induced hydrogen diffusion in metallic membranes. Int. J. Hydrogen Energy **1997**, *22* (1), 27.
395. Zhang, W.-S.; Zhang, X.-W.; Zhang, Z.-L. Steady concentration distribution of hydrogen in elastic membranes during hydrogen diffusion. J. Alloys Compd. **2000**, *302*, 258.
396. Zhang, W.-S.; Zhang, X.-W.; Zhang, Z.-L. Effects of self-induced stress on the steady concentration distribution of hydrogen in fcc metallic membranes during hydrogen diffusion. Phys. Rev. B **2000**, *62* (13), 8884.
397. Keizer, K.; Uhlhorn, R.J.R.; Zaspalis, V.T.; Burggraaf, A.J. Transport and related (gas and vapour) separation in ceramic membranes. Key Eng. Mater. **1991**, *61 & 62*, 143.
398. Wu, J.C.S.; Flowers, D.F.; Liu, P.K.T. High-temperature separation of binary gas mixtures using microporous ceramic membranes. J. Membr. Sci. **1993**, *77*, 85.
399. Barbieri, G.; Violante, V.; Drioli, E. Methane steam reforming analysis in a palladium-based catalytic membrane reactor. Ind. Eng. Chem. Res. **1997**, *36* (8), 3369.
400. Uemiya, S.; Kajiwara, M.; Kojima, T. Composite membranes of group VIII metal supported on porous alumina. AIChE J.: Ceram. Process. **1997**, *43* (11A), 2715.
401. Liu, Y.; Dixon, A.G.; Ma, Y.H.; Moser, W.R. Permeation of ethylbenzene and hydrogen through untreated and catalytically-treated alumina membranes. Sep. Sci. Technol. **1990**, *25* (13–15), 1511.
402. Sotirchos, S.V.; Burganos, V.N. Transport of gases in porous membranes. MRS Bull. **1999**, *24* (3), 41.
403. Schofield, R.W.; Fane, A.G.; Fell, C.J.D. Gas and vapour transport through microporous membranes. I. Knudsen–Poiseuille transition. J. Membr. Sci. **1990**, *53* (1–2), 159.
404. Datta, R.; Dechapanichkul, S.; Kim, J.S.; Fang, L.Y.; Uehara, H. A generalized model for the transport of gases in porous, non-porous, and leaky membranes I. Application to single gases. J. Membr. Sci. **1992**, *75*, 245.

405. Scott, D.S.; Dullien, F.A.L. Diffusion of ideal gases in capillaries and porous solids. AIChE J. **1962**, *8* (1), 113.

406. Smid, J.; Avci, C.G.; Günay, V.; Terpstra, R.A.; Eijk, J.P.G.M. Preparation and characterization of microporous ceramic hollow fibre membranes. J. Membr. Sci. **1996**, *112*, 85.

407. Sircar, S.; Rao, M.B. Estimation of surface diffusion through porous media. AIChE J. **1990**, *36* (8), 1249.

408. So, J.-H.; Yang, S.-M.; Park, S.B. Preparation of silica–alumina composite membranes for hydrogen separation by multi-step pore modifications. J. Membr. Sci. **1998**, *147*, 147.

409. Xomeritakis, G.; Lin, Y.-S. CVD synthesis and gas permeation properties of thin palladium/alumina membranes. AIChE J. **1998**, *44* (1), 174.

410. Liu, B.; Li, H.; Cao, Y.; Deng, J.-F.; Sheng, C.; Zhou, S. Preparation and characterization of Ni–P amorphous alloy/ceramic composite membrane. J. Membr. Sci. **1997**, *135*, 33.

411. Lee, S.-J.; Yang, S.-M.; Park, S.B. Synthesis of palladium impregnated alumina membrane for hydrogen separation. J. Membr. Sci. **1994**, *96*, 223.

412. Huckins, H.E.; Kammermeyer, K. The separation of gases by means of porous membranes. Chem. Eng. Prog. **1953**, *49* (4), 180.

413. Uhlhorn, R.J.R.; Keizer, K.; Burggraaf, A.J. Gas and surface diffusion in modified $\gamma$-alumina systems. J. Membr. Sci. **1989**, *46*, 225.

414. Schramm, O.; Seidel-Morgenstern, A. Comparing porous and dense membranes for the application in membrane reactors. Chem. Eng. Sci. **1999**, *54* (10), 1447.

415. Kim, J.; Lin, Y.S. Synthesis and oxygen-permeation properties of Thin YSZ/Pd composite membranes. AIChE J. **2000**, *46* (8), 1521.

416. Ackerman, F.J.; Koskinas, G.J. Permeation of hydrogen and deuterium through palladium–silver alloys. J. Chem. Eng. Data **1972**, *17* (1), 51.

417. Deng, J.; Cao, Z.; Zhou, B. Catalytic dehydrogenation of ethanol in a metal-modified alumina membrane reactor. Appl. Catal., A **1995**, *132* (1), 9.

418. Uemiya, S.; Kato, W.; Uyama, A.; Kajiwara, M.; Kojima, T.; Kikuchi, E. Separation of hydrogen from gas mixtures using supported platinum-group metal membranes. Sep. Purif. Technol. **2001**, *22–23*, 309.

419. Xue, D.; Deng, J.-F. Amorphous Ni–B alloy/ceramic composite membrane prepared by an improved electroless plating technique. Mater. Lett. **2001**, *47*, 271.

420. Cao, Y.; Liu, B.; Deng, J. Catalytic dehydrogenation of ethanol in Pd–M/$\gamma$–$Al_2O_3$ composite membrane reactors. Appl. Catal., A **1997**, *154* (1–2), 129.

421. Felter, T.E.; Stulen, R.H.; Koszykowski, M.L.; Gdowski, G.E.; Garrett,

B. Experimental and theoretical investigation of hydrogen diffusion on a metal surface. J. Vac. Sci. Technol., A **1989**, *7* (1), 104.

422. Eguchi, K.; Chai, M.-R.; Machida, M.; Arai, H. Metal dispersed porous alumina membrane for selective hydrogen permeation and its application to membrane reactor for methane steam reforming. Stud. Surf. Sci. Catal. **1994**, *92*, 251.
423. Eguchi, K.; Chai, M.-R.; Yamashita, Y.; Machida, M.; Arai, H. Selective hydrogen permeation through metal-dispersed porous alumina membrane. Stud. Surf. Sci. Catal. **1993**, *77*, 195.
424. Chai, M.; Machida, M.; Eguchi, K.; Arai, H. Promotion of methane steam reforming using ruthenium-dispersed microporous alumina membrane reactor. Chem. Lett. **1993** (1), 41.
425. Chai, M.; Yamashita, Y.; Machida, M.; Eguchi, K.; Arai, H. Preparation and characterization of metal-dispersed alumina membranes for selective separation of hydrogen. J. Membr. Sci. **1994**, *97*, 199.
426. Zaluski, L.; Zaluski, A.; Tessier, P.; Ström-Olsen, J.O.; Schulz, R. Catalytic effect of Pd on hydrogen absorption in mechanically alloyed $Mg_2Ni$, $LaNi_5$ and FeTi. J. Alloys Compd. **1995**, *217*, 295.
427. Liu, B.; Wu, G.; Niu, G.; Deng, J.-F. Rh-modified alumina membranes: Preparation, characterization and reaction studies. Appl. Catal., A **1999**, *185*, 1.
428. Kajiwara, M.; Uemiya, S.; Kojima, T. Stability and hydrogen permeation behavior of supported platinum membranes in presence of hydrogen sulfide. Int. J. Hydrogen Energy **1999**, *24* (9), 839.
429. Kajiwara, M.; Uemiya, S.; Kojima, T.; Kikuchi, E. Hydrogen permeation properties through composite membranes of platinum supported on porous alumina. Catal. Today **2000**, *56* (1–3), 65.
430. Kajiwara, M.; Uemiya, S.; Kojima, T.; Kikuchi, E. Rhodium- and iridium-dispersed porous alumina membranes and their hydrogen permeation properties. Catal. Today **2000**, *56* (1–3), 83.
431. Rubin, L.R. Seal for Thin Tubing. US Patent 3,437,357, 1969.
432. Clark, E.A.; Dauchess, D.A.; Heung, L.K.; Rabun, R.L.; Motyka, R.T. *SRS History and Experience with Palladium Diffusers, DE96002953*; 1995.
433. Raftopoulos, S.; Gentile, C.; LaMarche, P.; Langford, J. Operational experience of the tritium purification system. Fusion Technol. **1996**, *30* (3), 922.
434. Juda, W. Diffusion-bonded palladium–copper alloy framed membrane for pure hydrogen generators and the like and method of preparing the same. US Patent 5,904,754, May 18, 1999.
435. Ito, Y.; Sakai, H. A simple and reusable metal sample holder for hydrogen permeation experiments. Rev. Sci. Instrum. **1990**, *62* (1), 253.

436. Quicker, P.; Höllein, V.; Dittmeyer, R. Catalytic dehydrogenation of hydrocarbons in palladium composite membrane reactors. Catal. Today **2000**, *56* (1–3), 21.
437. Akiyama, S.; Mizuta, H.; Anzai, H.; Kusakabe, K.; Morooka, S. In *Preparation of Gas Separation Membranes Supported on α-alumina Porous Hollow Fibers*, Proc. 5th Intl. Conf. Inorganic Membr., Nagoya, Japan, June 22–26, 1998; 398.
438. Chaklader, A.C.D.; Armstrong, A.M.; Misra, S.K. Interface reactions between metals and ceramics: IV, wetting of sapphire by liquid copper–oxygen alloys. J. Am. Ceram. Soc. **1968**, *51* (11), 630.
439. Rubin, L.R. Apparatus and method for the production of pure hydrogen from a hydrogen-containing crude gas. US Patent 4,472,176, Sep. 18, 1984.
440. Benson, S. *Ceramics for Advanced Power Generation*; IEA Coal Research: London, 2000.
441. Mercea, P.-V.; Mecea, V. Gas separation through a high-flux asymmetric polymer membrane metallized with palladium. Gas Sep. Purif. **1991**, *5*, 267.
442. McCool, B.A.; Lin, Y.S. Nanostructured thin palladium–silver membranes: Effects of grain size on gas permeation properties. J. Mater. Sci. **2001**, *36*, 3221.
443. Ali, J.K.; Newson, E.J.; Rippin, D.W.T. Deactivation and regeneration of Pd–Ag membranes for dehydrogenation reactions. J. Membr. Sci. **1994**, *89*, 171.
444. Roshan, N.R.; Mishchenko, A.P.; Ployakova, V.P.; Parfenova, N.I.; Savitsky, E.M.; Voitekhova, E.A.; Gryaznov, V.M.; Sarylova, M.E. The effect of the surface state on the hydrogen permeability and the catalytic activity of palladium alloy membranes. J. Less-Common Met. **1983**, *89*, 423.
445. Yoshida, H.; Konishi, S.; Naruse, Y. Effects of impurities on hydrogen permeability through palladium alloy membranes at comparatively high pressures and temperatures. J. Less-Common Met. **1983**, *89*, 429.
446. Sakamoto, F.; Kinari, Y.; Chen, F.L.; Sakamoto, Y. Hydrogen permeation through palladium alloy membranes in mixture gases of 10% nitrogen and ammonia in the hydrogen. Int. J. Hydrogen Energy **1997**, *22* (4), 369.
447. Conrad, H.; ERtl, G.; Latta, E.E. Coadsorption of hydrogen and carbon monoxide on a Pd (110) surface. J. Catal. **1974**, *35*, 363.
448. Ali, J.K.; Hasler, P.; Newson, E.J.; Rippin, D.W.T. Irreversible poisoning of Pd–Ag membranes. Int. J. Hydrogen Energy **1994**, *19* (11), 877.
449. Edlund, D.J.; Pledger, W.A. Catalytic platinum-based membrane reactor for removal of $H_2S$ from natural gas streams. J. Membr. Sci. **1994**, *94*, 111.

450. Edlund, D.J.; Pledger, W.A. Thermolysis of hydrogen sulfide in a metal-membrane reactor. J. Membr. Sci. **1993**, *77*, 255.

451. Edlund, D. In *A Membrane Reactor for $H_2S$ Decomposition*, Advanced Coal-fired Power Systems ’96 Review Meeting, Morgantown, West Virginia, US, Jul. 16–18, 1996.

452. Sutyagina, A.A.; Perepelitsa, V.A. Behavior of palladium electrodes poisoned with sulfur during cyclic anodic-cathodic polarization. Sov. Electrochem. (Elektrokhimiya) **1984**, *20* (8), 1036.

453. Dannetun, H.; Wilz, N.L.; Petersson, L.-G. The study of alcohol induced hydrogen permeation in a catalytic membrane reactor. Surf. Sci. **1996**, *357*, 804.

454. Chabot, J.; Lecomte, J.; Grumet, C.; Sannier, J. Fuel clean-up system: Poisoning of palladium–silver membranes by gaseous impurities. Fusion Technol. **1988**, *14*, 614.

455. Drioli, E.; Violante, V.; Basile, A. In *Membrane Separation Processes in the Fusion Fuel Cycle*, Proc. 1990 Intl. Congress on Membranes and Membrane Processes, 1990; 1040.

456. Sakamoto, Y.; Chen, F.L.; Kinari, Y.; Sakamoto, F. Effect of carbon monoxide on hydrogen permeation in some palladium-based alloy membranes. Int. J. Hydrogen Energy **1996**, *21* (11/12), 1017.

457. Wilzén, L.; Petersson, L.-G. A membrane reactor for permeation and catalytic reaction studies. Vacuum **1995**, *46* (8–10), 1237.

458. Ziemecki, S.B.; Jones, G.A.; Swarzfager, D.G. Coexistence of hydrogen and carbon solutes in the palladium lattice. J. Less-Common Met. **1987**, *131*, 157.

459. Chen, F.L.; Kinari, F.; Sakamoto, Y.; Nakayama, Y.; Sakamoto, Y. Hydrogen permeation through palladium-based alloy membranes in mixtures of 10% methane and ethylene in the hydrogen. Int. J. Hydrogen Energy **1996**, *21* (7), 555.

460. Yeung, K.L.; Wolf, E.E. Scanning tunneling microscopy study of Pd thin film catalyst. I. Effect of the adsorbates and surface reaction on the film structure. J. Catal. **1993**, *143* (2), 409.

461. Galuszka, J.; Pandey, R.N.; Ahmed, S. Methane conversion to syngas in a palladium membrane reactor. Catal. Today **1998**, *46*, 83.

462. Behm, R.J.; Penka, V.; Cattania, M.-G.; Christmann, K.; Ertl, G. Evidence for ‘‘subsurface’’ hydrogen on Pd(110): An intermediate between chemisorbed and dissolved species. J. Chem. Phys. **1983**, *78* (12), 7486.

463. Zolfaghari, A.; Villiard, F.; Chayer, M.; Jerkiewicz, G. Hydrogen adsorption on Pt and Rh electrodes and blocking of adsorption sites by chemisorbed sulfur. J. Alloys Compd. **1997**, *253–254*, 481.

464. Wilke, S.; Scheffler, M. Mechanism of poisoning the catalytic activity of Pd(100) by a sulfur adlayer. Phys. Rev. Lett. **1996**, *76* (18), 3380.

465. Peden, H.F.; Kay, B.D.; Goodman, D.W. Kinetics of hydrogen absorption by chemically modified Pd(110). Surf. Sci. **1986**, *175*, 215.
466. Eriksson, M.; Ekedahl, L.-G. Real time measurements of hydrogen desorption and absorption during CO exposures of Pd: Hydrogen sticking and dissolution. Appl. Surf. Sci. **1998**, *133*, 89.
467. Amandusson, H.; Ekedahl, L.-G.; Dannetun, H. The effect of CO and $O_2$ on hydrogen permeation through a palladium membrane. Appl. Surf. Sci. **2000**, *153*, 259.
468. Gravil, P.A.; Toulhoat, H. Hydrogen, sulphur and chlorine coadsorption on Pd(111): A theoretical study of poisoning and promotion. Surf. Sci. **1999**, *430*, 176.
469. Koffler, S.A.; Hudson, J.B.; Ansell, G.S. Hydrogen permeation through alpha–palladium. Trans. Metall. Soc. AIME **1969**, *245*, 1735.
470. Bezvorotnyi, P.V.; Katsnel, M.G. Aspects of the poisoning of palladium catalysts by sulfur compounds during gas-phase hydrogenation. J. Appl. Chem. USSR (Zh. Prikl. Khim.) **1991**, *63* (8), 1742.
471. Amano, M.; Nishimura, M.; Komaki, M.; Shida, M. Hydrogen Separating Membrane. JP Patent 1262924, 1989.
472. Edlund, D.J.; McCarthy, J. The relationship between intermetallic diffusion and flux decline in composite–metal membranes: Implications for achieving long membrane lifetime. J. Membr. Sci. **1995**, *107*, 147.
473. Abdullaev, R.M.; Tontegode, A.Y. Effect of carbon dissolution and segregation in palladium on the catalytic, optical, and electric properties. Sov. Phys. Tech. Phys. (Zh. Tekh. Fiz.) **1980**, *25* (3), 346.
474. Stachurski, J.; Frackiewicz, A. A new phase in the Pd–C system formed during the catalytic hydrogenation of acetylene. J. Less-Common Met. **1985**, *108*, 249.
475. Siller, R.H.; Oates, W.A.; McLellan, R.B. The solubility of carbon in palladium and platinum. J. Less-Common Met. **1968**, *16*, 71.
476. Ziemecki, S.B.; Jones, G.A. Interstitial carbon in palladium. J. Catal. **1985**, *95*, 621.
477. Ziemecki, S.B.; Jones, G.A.; Swartzfager, D.G.; Harlow, R.L. Formation of interstitial Pd–C phase by interaction of ethylene, acetylene, and carbon monoxide with palladium. J. Am. Chem. Soc. **1985**, *107*, 4547.
478. Harris, J.R. Coated Diffusion Membrane and Its Use. US Patent 4,536,196, Aug. 20, 198.
479. Harris, J.R. Palladium or a Palladium Alloy Hydrogen Diffusion Membrane Treated with a Volatile Compound of Silicon is Used to Separate Hydrogen from a Mixture of it with a Hydrocarbon. US Patent 4,313, 013, Jan. 26, 1982.
480. Collins, J.P. Rebuttal to the comments of J. Gunther Cohn on ‘‘catalytic

dehydrogenation of propane in hydrogen permselective membrane reactors''. Ind. Eng. Chem. Res. **1997**, *36*, 2876.

481. Cohn, J.G. Comments on ''catalytic dehydrogenation of propane in hydrogen permselective membrane reactors''. Ind. Eng. Chem. Res. **1997**, *36*, 2875.
482. Skakunova, E.V.; Ermilova, M.M. Hydrogenolysis of propane on a palladium–ruthenium alloy membrane catalyst. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1988**, *5*, 986.
483. Gryaznov, V.M.; Ermilova, M.M.; Orekhova, N.V. Reconstruction of the surface layer of platinum group metals in the thermal treatment in various gases and propane hydrogenolysis. Russ. Chem. Bull. (Izv. Akad. Nauk, Ser. Khim.) **1998**, *47* (6), 1067.
484. Glazunov, G.P.; Kosik, N.A.; Yuferov, V.B.; Svinarenko, A.P.; Azhazha, V.M. Possible effects of sputtering of materials in thermonuclear power plants on the operation of membrane pumps. Sov. Phys. Tech. Phys. (Zh. Tekh. Fiz.) **1981**, *26* (10), 1251.
485. Koonce, J.; Yoshida, H.; Kveton, O.; Horikiri, H.; Haange, R. Design of ITER plasma exhast processing systems. Fusion Technol. **1995**, *28*, 630.
486. Manga, I.I.; Kondrasheva, V.S.; Vasil'ev, Y.B.; Gryaznov, V.M. Mercury adsorption effect on hydrogen evolution reaction on platinum and palladium. Russ. J. Electrochem. (Elektrokhimiya) **1993**, *29* (4), 486.
487. Gryaznov, V.M.; Smirnov, V.S.; Slin'ko, M.G. In *Binary Palladium Alloys as Selective Membrane Catalysts*, Proc. 6th Intl. Congress on Catal., London, England, 1976; Bond, G.C., Wells, P.B., Tompkins, F.C., Eds.; The Chemical Society: London, 894.
488. Yamakawa, K.; Ege, M.; Ludescher, B.; Hirscher, M.; Kronmüller, H. Hydrogen permeability measurement through Pd, Ni and Fe membranes. J. Alloys Compd. **2001**, *321*, 17.
489. Yang, L.; Sakai, O.; Kosaka, S.; Kawae, T.; Takahashi, T. In *Experimental Study on Hydrogen Permeation and Surface Property of Pd–Ag/Ceramic Composite Membranes*, Proc. 5th Intl. Conf. Inorganic Membr., Nagoya, Japan, June 22–26, 1998; 482.
490. Serfass, E.J. Activated Surfaces Useful in the Production of Hydrogen. US Patent 3,448,035, Jun. 3, 1969.
491. Radjabov, T.D.; Alimova, L.Y.; Sharudo, A.V. Low voltage hydrogen plasma interaction with palladium surface. J. Nucl. Mater. **1984**, *125*, 326.
492. Aggarwal, S.; Monga, A.P.; Perusse, S.R.; Ramesh, R.; Ballarotto, V.; Williams, E.D.; Chalamala, B.R.; Wei, Y.; Reuss, R.H. Spontaneous ordering of oxide nanostructures. Science **2000**, *287*, 2235.
493. Wang, D.; Clewley, J.D.; Flanagan, T.B.; Balasubramaniam, R.;

Shanahan, K.L. Enhanced rates of hydrogen absorption resulting from oxidation of Pd or internal oxidation of Pd–Al alloys. J. Alloys Compd. **2000**, *298*, 261.

494. Uchikawa, H.; Okazaki, T.; Sato, K. New technique of activating palladium surface for absorption of hydrogen or deuterium. Jpn. J. Appl. Phys. **1993**, *32* (1 (11A)), 5095.

495. Dobrokhotov, V.G.; Pavlova, L.F.; Gryaznov, V.M. Effect of hydrogen on the adsorption of cyclohexane vapor on a palladium–ruthenium alloy. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1983**, *32* (5), 890.

496. Ustinova, T.S.; Smirnov, V.S.; Gryaznov, V.M.; Antoshin, G.V.; Shapiro, E.S.; Onwodi, F.A.; Shimulis, V.I.; Minachev, K.M. Influence of a catalytic reaction on the surface composition and roughness factor of palladium–ruthenium alloys. React. Kinet. Catal. Lett. (Soobshch. Kinet. Katal.) **1978**, *9* (2), 227.

497. Clewley, J.D.; Curran, T.; Flanagan, T.B.; Oates, W.A. Thermodynamic properties of hydrogen and deuterium dissolved in palladium at low concentrations over a wide temperature range. J. Chem. Soc., Faraday Trans. 1 **1973**, *69*, 449.

498. Onwodi, F.A.; Shimulis, V.I.; Gryaznov, V.M. Adsorption properties of membrane catalysts. React. Kinet. Catal. Lett. (Soobshch. Kinet. Katal.) **1977**, *6* (1), 51.

499. Farrauto, R.J.; Hobson, M.C.; Kennelly, T.; Waterman, E.M. Catalytic chemistry of supported palladium for combustion of methane. Appl. Catal., A **1992**, *81*, 227.

500. Chaston, J.C. Reactions of oxygen with the platinum metals. III—the oxidation of palladium. Platinum Met. Rev. **1965**, *9* (4), 126.

501. Lee, K.-H.; Wolf, E.E. Scanning probe microscopy studies of the activation and deactivation of Pd thin film catalysts. Stud. Surf. Sci. Catal. **1994**, *88*, 69.

502. Ermilova, M.M.; Orekhova, N.V.; Skakunova, E.V.; Gryaznov, V.M. Changes in the catalytic activity and hydrogen permeability of a palladium–ruthenium alloy membrane catalyst under the influence of reagents. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1988**, *37* (4), 637.

503. Maganyuk, A.P.; Gizhevskii, S.F.; Gryaznov, V.M. Selective hydrogenation of dehydrolinalool and dehydroisophytol in a liquid film moving over Pd–Ru foil. Russ. J. Phys. Chem. **1998**, *72* (8), 1244.

504. Mikhalenko, N.N.; Khrapova, E.V.; Gryaznov, V.M. Mutual relationship of the hydrogen permeability of membrane catalysts and of the composition of the hydrogenation products of cyclopentadiene. Russ. J. Phys. Chem. **1986**, *60* (9), 1317.

505. Ledoux, M.J.; Gault, F.G. Correlation between surface structure and reaction mechanisms: Reactions of olefins on nickel and palladium films. J. Catal. **1979**, *60*, 15.

506. Bryden, K.J.; Ying, J.Y. Thermal stability and hydrogen absorption characteristics of palladium–yttrium nanoalloys. Acta Mater. **1996**, *44* (9), 3847.

507. Kirchheim, R.; Kownacka, I.; Filipek, S.M. Hydrogen segregation at grain boundaries in nanocrystalline nickel. Scr. Metall. **1993**, *28*, 1229.

508. Mütschele, T.; Kirchheim, R. Segregation and diffusion of hydrogen in grain boundaries of palladium. Scr. Metall. **1987**, *21*, 135.

509. Natter, H.; Schmeizer, M.; Janßen, S.; Hempelmann, R. Nanocrystalline metals and oxides I: Pulsed electrodeposition. Ber. Bunsen-Ges. **1997**, *101* (11), 1706.

510. Stuhr, U.; Wipf, H.; Andersen, K.H.; Hahn, H. Neutron scattering study of the vibrational behaviour of H-doped nanocrystalline Pd. Physica B **2000**, *276–278*, 882.

511. Stuhr, U.; Striffler, T.; Wipf, H.; Natter, H.; Wettmann, B.; Janssen, S.; Hempelmann, R.; Hahn, H. An investigation of hydrogen diffusion in nanocrystalline Pd by neutron spectroscopy. J. Alloys Compd. **1997**, *253–254* (1–2), 393.

512. Janßen, S.; Natter, H.; Hempelmann, R.; Striffler, T.; Stuhr, U.; Wipf, H.; Hahn, H.; Cook, J.C. Hydrogen diffusion in nanocrystalline Pd by means of quasielastic neutron scattering. Nanostruct. Mater. **1997**, *9*, 579.

513. Natter, H.; Wettmann, B.; Heisel, B.; Hempelmann, R. Hydrogen in nanocrystalline palladium. J. Alloys Compd. **1997**, *253–254*, 84.

514. Heinze, S.; Vuillemin, B.; Colson, J.-C.; Giroux, P.; Leterq, D. Relation between grain size and hydrogen diffusion coefficient in an industrial Pd-23% Ag alloy. Solid State Ionics **1999**, *122*, 51.

515. Doyle, D.M.; Palumbo, G.; Aust, K.T.; El-Sherik, A.M.; Erb, U. The influence of intercrystalline defects on hydrogen activity and transport in nickel. Acta Metall. Mater. **1995**, *43* (8), 3027.

516. Harris, T.M.; Latanision, R.M. Grain boundary diffusion of hydrogen in nickel. Metall. Trans. A **1991**, *22A*, 351.

517. Palumbo, G.; Doyle, D.M.; El-Sherik, A.M.; Erb, U.; Aust, K.T. Intercrystalline hydrogen transport in nanocrystalline nickel. Scr. Metall. **1991**, *25* (3), 679.

518. Bucur, R.V.; Ersson, N.O.; Tong, X.Q. Solubility and diffusivity of hydrogen in palladium and $Pd_{77}Ag_{23}$ containing lattice defects. J. Less-Common Met. **1991**, *172–174*, 748.

519. Hagi, H. Diffusion coefficient of hydrogen in palladium films prepared by RF sputtering. Mater. Trans., JIM **1990**, *31* (11), 954.

520. Revkevich, G.P.; Katsnel'son, A.A.; Khristov, V. Time and orientation dependence in hydrogen-saturated palladium outgassing rates. Moscow Univ. Phys. Bull. **1988**, *43* (3), 74.
521. Klotsman, S.M. Diffusion in nanocrystalline materials. Phys. Met. Metallogr. **1993**, *75* (4), 386.
522. Striffler, T.; Stuhr, U.; Wipf, H.; Hahn, H.; Egelhaaf, S. The microstructure of hydrogen- and deuterium-doped nanocrystalline palladium studied by small-angle neutron scattering. Eur. Phys. J. B **2000**, *17*, 245.
523. Striffler, T.; Stuhr, U.; Wipf, H.; Hahn, H.; Egelhaaf, S. Small-angle neutron scattering on hydrogen- and deuterium-doped nanocrystalline palladium. Physica B **2000**, *276–278*, 880.
524. Lee, M.W.; Wolf, R.J.; Ray, J.R. Atomistic calculations of hydrogen loading in palladium. J. Alloys Compd. **1995**, *231*, 343.
525. Kirchheim, R. Interaction of hydrogen with dislocations in palladium—I. Activity and diffusivity and their phenomenological interpretation. Acta Metall. **1981**, *29*, 835.
526. Kuji, T.; Uchida, H.; Sato, M.; Cui, W. Thermodynamic properties of hydrogen in fine Pd powders. J. Alloys Compd. **1999**, *293–295*, 19.
527. Eastman, J.A.; Thompson, L.J.; Kestel, B.J. Narrowing of the palladium–hydrogen miscibility gap in nanocrystalline palladium. Phys. Rev. B **1993**, *48* (1), 84.
528. Wang, D.; Flanagan, T.B.; Balasubramaniam, R. Hydrogen solubility as a probe for dislocation formation, rearrangement and annhilation in Pd and Pd/$Al_2O_3$ composites. Scr. Mater. **1999**, *41* (5), 517.
529. Sakamoto, Y.; Tabaru, N. Diffusivity and solubility of hydrogen in annealed and cold rolled specimens of palladium. J. Jpn. Inst. Met. **1981**, *45* (10), 1048.
530. Horkans, J. Film thickness effects on hydrogen sorption at palladium electrodes. J. Electroanal. Chem. **1980**, *106*, 245.
531. Flanagan, T.B.; Noh, H. Thermodynamics and hysteresis for hydrogen solution and hydride formation in Pd–Ni Alloys. Z. Naturforsch., A: Phys. Sci. **1995**, *50*, 475.
532. Flanagan, T.B.; Lynch, J.F. The effect of lattice defects on hydrogen solubility in palladium II. Interpretation of solubility enhancements. J. Less-Common Met. **1976**, *49*, 25.
533. Gol'tsov, V.A.; Lobanov, B.A. Changes induced in the substructure of palladium by hydrogen-phase hardening and subsequent annealing. Sov. Phys. Dokl. **1985**, *30* (7), 613.
534. Kotelva, R.V.; Glukhova, J.L. Form changing of palladium plate under hydrogen treatment. Int. J. Hydrogen Energy **1997**, *22* (2/3), 175.
535. Spivak, L.V.; Skryabina, N.Y.; Kuznetsova, Y.V.; Gel'd, P.V. Stress

relaxation and creep during hydrogenation of palladium. Phys. Met. Metallogr. **1987**, *64* (4), 157.

536. Storms, E.; Talcott-Storms, C. The effect of hydriding on the physical structure of palladium and on the release of contained tritium. Fusion Technol. **1991**, *20* (2), 246.
537. Timofeyev, N.I.; Gromov, V.I.; Berseneva, F.N.; Gol'tsov, V.A. Influence of solute hydrogen on the mechanical properties of palladium. Phys. Met. Metallogr. **1980**, *49* (4), 173.
538. Takagi, S.; Sugeno, T. Plastic deformation of Pd–H alloys. Jpn. J. Appl. Phys. **1965**, *4* (10), 772.
539. Rodina, A.A.; Gurevich, M.A.; Doronicheva, N.I. The cause of the change in the stability of certain palladium–rhodium alloys on interaction with hydrogen. Russ. J. Phys. Chem. **1968**, *42* (7), 959.
540. Revkevich, G.P.; Katsnel'son, A.A.; Khristov, V.M. Effect of hydrogen absorption on short range order in the alloy Pd + 15 at% Cu. Russ. Metall. (Izv. Akad. Nauk SSSR, Met.) **1990**, *4*, 182.
541. Kodes, Y.S.; Zakharov, A.B.; Timofeyev, M.I.; Gel'd, P.V. Internal friction and spontaneous deformation due to the direct and reverse hydride transformation in palladium. Phys. Met. Metallogr. **1989**, *67* (6), 123.
542. Scholtus, N.A.; Hall, W.K. Hysteresis in the palladium–hydrogen system. J. Chem. Phys. **1963**, *39* (4), 868.
543. Kagan, G.Y.; Koshelva, V.Y.; Gel'd, P.V.; Kurumchina, S.K. Influence of $\alpha \rightarrow \gamma$ phase transformation on the physico-mechanical properties of palladium and its alloys. Phys. Met. Metallogr. **1978**, *45* (5), 109.
544. Bucur, R.V. Two-channel mechanism for diffusion of hydrogen in palladium and $Pd_{77}Ag_{23}$-alloy. Scr. Metall. **1993**, *29*, 457.
545. Kajiwara, M.; Uemiya, S.; Kojima, T.; Kikuchi, E. In *Hydrogen Permeation Through Composite CVD Membranes of Group-VIII Metals and Porous Alumina*, Proc. 5th Intl. Conf. Inorganic Membr., Nagoya, Japan, June 22–26, 1998; 250.
546. Sakamoto, Y.; Hirata, S.; Nishikawa, H. Diffusivity and solubility of hydrogen in Pd–Ag and Pd–Au alloys. J. Less-Common Met. **1982**, *88*, 387.
547. Dong, W.; Ledentu, V.; Sautet, P.; Eichler, A.; Hafner, J. Hydrogen absorption on palladium: A comparative theoretical study of different surfaces. Surf. Sci. **1998**, *411*, 123.
548. Conrad, H.; Ertl, G.; Latta, E.E. Adsorption of hydrogen on palladium single crystal surfaces. Surf. Sci. **1974**, *41*, 435.
549. Polyakova, V.P.; Roshan, N.R.; Parfenova, N.I. Recrystallization of palladium alloyed with ruthenium. Met. Sci. Heat Treat. Met. (Metalloved. Term. Obrab. Met.) **1980**, *22* (2), 154.

550. Bystritskii, V.M.; Gur'yanov, V.G.; Ionesyan, I.A.; Latyshev, V.V.; Malek, M.P.; Nikolaev, V.L.; Rivkis, L.A.; Stolupin, V.A. Membrane filter for diffusion separation and production of ultrahigh-purity hydrogen isotopes. Instrum. Exp. Tech. (Prib. Tekh. Eksp.) **1991**, *34* (1), 227.
551. Clifford, J.E.; Kolic, E.S.; Faust, C.L. Water electrolysis with a hydrogen-diffusion cathode. AIChE Symp. Ser. **1966**, *62*, 43.
552. Gol'tsov, V.A.; Machikina, I.Y.; Timofeev, N.I. Recrystallization of hydrogen-phase-hardened palladium. Dokl. Akad. Nauk SSSR **1979**, *24* (7), 571.
553. Gol'tsov, V.A.; Kirillov, V.A.; Karnaukh, O.I.; Volynskaya, V.G.; Gorban, S.V. Recovery of mechanical and physical properties of hydrogen phase hardened palladium. Phys. Met. Metallogr. **1982**, *54* (2), 149.
554. Noh, H.; Luo, W.; Flanagan, T.B. The effect of annealing pretreatment of Pd–Rh alloys on their hydrogen solubilities and thermodynamic parameters for $H_2$ solution. J. Alloys Compd. **1993**, *196*, 7.
555. Hughes, D.T.; Evans, J.; Harris, I.R. The influence of order on hydrogen diffusion in the solid solution alloys Pd—5.75at.%Ce and Pd—8at.%Y. J. Less-Common Met. **1980**, *74*, 255.
556. Doyle, M.L.; Wileman, R.C.J.; Harris, I.R. Electrical resistance and hydrogen solubility anomalies in a Pd—8at.%Y solid solution alloy. J. Less-Common Met. **1987**, *130* (130), 79.
557. Gol'tsov, V.A.; Gel'd, P.V.; Kagan, G.E. Influence of ordering and alloying on the hydrogen parameters of alloys. Phys. Met. Metallogr. **1971**, *32* (2), 70.
558. Makarov, V.M.; Veselov, I.N.; Vandyshev, A.B.; Timofeev, N.I. Results of basic and applied research in hydrogen membrane technology. Chem. Pet. Eng. (Khim. Neft. Mashinostr.) **1996**, *32* (5), 399.
559. Wileman, R.C.; Harris, I.R. The permeability behaviour of protium and deuterium through a Pd-7.5at.%Y membrane. J. Less-Common Met. **1985**, *109*, 367.
560. Yeung, K.L.; Christiansen, S.C.; Varma, A. Palladium composite membranes by electroless plating technique: Relationships between plating kinetics, film microstructure and membrane performance. J. Membr. Sci. **1999**, *159*, 107.
561. Lobanov, V.V.; Klyuyeva, I.B.; Kagan, G.Y.; Ryabov, R.A.; Guk, Y.N.; Gel'd, P.V. Influence of atomic ordering on the behaviour of hydrogen in the alloy Pd-20 W. Phys. Met. Metallogr. **1979**, *47* (3), 176.
562. Lobanov, V.V.; Ryadov, R.A.; Gel'd, P.V.; Kagan, G.E. The activation energy of hydrogen diffusion in fcc metals and alloys. Sov. Phys. Tech. Phys. (Zh. Tekh. Fiz.) **1980**, *25* (6), 732.
563. Lobanov, V.V.; Kagan, G.E.; Gel'd, P.V.; Ryabov, R.A.; Guk, Y.N.

Hydrogen permeability of palladium–tungsten alloys. Russ. J. Phys. Chem. **1978**, *52* (10), 1443.

564. Guk, Y.N.; Kagan, G.E.; Lobanov, V.V.; Levin, E.S. Solubility of hydrogen in dilute solid solutions of nickel and platinum in palladium. Russ. J. Phys. Chem. **1982**, *56* (5), 712.
565. Guk, Y.N.; Kagan, G.E.; Lobanov, V.V.; Levin, E.S.; Gel'd, P.V. Hydrogen permeability of palladium–platinum alloys. Russ. Metall. (Izv. Akad. Nauk SSSR, Met.) **1981** (6), 187.
566. Gryaznov, V.M.; Gul'yanova, S.G.; Serov, Y.M.; Yagodovskii, V.D. The hydrogenation of $CO_2$ on a nickel-coated palladium–ruthenium membrane catalyst. Russ. J. Phys. Chem. **1981**, *55* (5), 730.
567. Jayaraman, V.; Lin, Y.S.; Pakala, M.; Lin, R.Y. Fabrication of ultrathin metallic membranes on ceramic supports by sputter deposition. J. Membr. Sci. **1995**, *99*, 89.
568. Wu, L.-Q.; Xu, N.; Shi, J. Preparation of a palladium composite membrane by an improved electroless plating technique. Ind. Eng. Chem. Res. **2000**, *39* (2), 342.
569. Paglieri, S.N.; Foo, K.Y.; Way, J.D.; Collins, J.P.; Harper-Nixon, D.L. A new preparation technique for Pd/alumina membranes with enhanced high temperature stability. Ind. Eng. Chem. Res. **1999**, *38* (5), 1925.
570. Nagamoto, H.; Inoue, H. Sorption and desorption of hydrogen on palladium sheet. J. Chem. Soc. Jpn. (Nippon Kagaku Kaishi) **1977**, *9*, 1264.
571. Lewis, F.A. The palladium–hydrogen system: Structures near phase transition and critical points. Int. J. Hydrogen Energy **1995**, *20* (7), 587.
572. Flanagan, T.B.; Sakamoto, Y. Hydrogen in disordered and ordered palladium alloys. Int. J. Hydrogen Energy **1994**, *19* (2), 151.
573. Lewis, F.A. The palladium–hydrogen system. Platinum Met. Rev. **1982**, *26* (1), 20.
574. Lewis, F.A. The palladium–hydrogen system: Part II of a survey of features. Platinum Met. Rev. **1982**, *26* (2), 70.
575. Lewis, F.A. The palladium–hydrogen system: Part III: Alloy systems and hydrogen permeation. Platinum Met. Rev. **1982**, *26* (3), 121.
576. Antler, M. The application of palladium in electronic connectors. Platinum Met. Rev. **1982**, *26*, 106.
577. Chen, F.L.; Kinari, Y.; Sakamoto, Y. The $\alpha/\beta$ hydrogen miscibility gaps in hydrogenated Pd–Y–In(Sn, Pb) ternary alloys. J. Alloys Compd. **1994**, *205*, 119.
578. Chen, S.-K.; Wan, C.-M.; Liu, E.-H.; Chu, S.-B.; Liang, C.-Y.; Yuan, L.-J.; Wan, C.-C. The microstructure of electrolytically deuterium loaded palladium rods. Fusion Technol. **1996**, *29*, 302.
579. Belash, V.P.; Klimova, I.N.; Kormilets, V.I. Electronic structure of PdH

studied by x-ray photoelectron spectroscopy. Phys. Met. Metallogr. **1997**, *84* (2), 134.

580. De Ninno, A.; La Barbera, A.; Violante, V. Deformations induced by high loading ratios in palladium–deuterium compounds. J. Alloys Compd. **1997**, *253–254*, 181.
581. Wise, M.L.H.; Farr, J.P.G.; Harris, I.R. X-ray studies of the α/β miscibility gaps of some palladium solid solution–hydrogen systems. J. Less-Common Met. **1975**, *41*, 115.
582. Hunter, J.B. A new hydrogen purification process. Platinum Met. Rev. **1960**, *4* (4), 130.
583. Sakamoto, Y.; Yuwasa, K.; Hirayama, K. X-ray investigation of the absorption of hydrogen by several palladium and nickel solid solution alloys. J. Less-Common Met. **1982**, *88*, 115.
584. Tovbin, Y.K.; Votyakov, E.V. Evaluation of the influence of dissolved hydrogen on mechanical properties of palladium. Phys. Solid State (Fiz. Tverd. Tela) **2000**, *42* (7), 1192.
585. Bellanger, G. Embrittlement of palladium and palladium–silver alloy cathode membranes by tritium. Fusion Technol. **1995**, *27*, 36.
586. Goltsov, V.A. The effects of hydrogen on the physical properties of palladium. Platinum Met. Rev. **1999**, *43* (3), 116.
587. Wolf, R.F.; Lee, M.W. Pressure-composition isotherms for nanocrystalline palladium hydride. Phys. Rev. Lett. **1994**, *73* (4), 557.
588. Votyakov, E.V.; Vasyutkin, N.F.; Senyavin, M.M.; Tovbin, Y.K. The effect of included hydrogen on the motion parameters of edge dislocations in palladium membranes. Prot. Met. (Zashch. Met.) **2001**, *37* (1), 53.
589. Aoki, K.; Ogata, Y.; Kusakabe, K.; Morooka, S. Applicability of palladium membrane for the separation of protium and deuterium. Int. J. Hydrogen Energy **1998**, *23* (5), 325.
590. Tovbin, Y.K.; Votyakov, E.V. Effect of interstitial hydrogen on the properties of palladium membranes. Russ. J. Phys. Chem. **2001**, *75* (4), 640.
591. Lewis, F.A. Hydrogen in palladium and palladium alloys. Int. J. Hydrogen Energy **1996**, *21* (6), 461.
592. Jewett, D.N.; Makrides, A.C. Diffusion of hydrogen through palladium and palladium–silver alloys. Trans. Faraday Soc. **1965**, *61* (505), 932.
593. Bellanger, G.; Rameau, J.J. Determination of tritium adsorption and diffusion parameters in a palladium–silver alloy by electrochemical impedance analysis. Fusion Technol. **1997**, *32*, 94.
594. Darling, A.S.; Yorke, J.M. The ruthenium–palladium system. Platinum Met. Rev. **1960**, *4* (3), 104.

595. Carson, A.W.; Lewis, F. Pressure-composition isotherms for the Pd + Ag + H system. Trans. Faraday Soc. **1967**, *63*, 1453.
596. Zhang, W.; Luo, S.; Flanagan, T.B. Hydrogen solution in homogeneous Pd–Fe alloys. J. Alloys Compd. **1999**, *293–295*, 1.
597. Sakamoto, Y.; Baba, K.; Flanagan, T.B. The effect of alloying of palladium on the hydrogen–palladium miscibility gap. Z. Phys. Chem. N.F. **1988**, *158*, 223.
598. Züchner, H.; Rauf, T. Electrochemical isotherm measurements on the Pd–H and PdAg–H systems. J. Less-Common Met. **1991**, *172–174*, 816.
599. Wicke, E.; Frölich, K. Electronic and elastic effects in the phase diagrams of binary Pd alloy hydrides. Z. Phys. Chem. N.F. **1989**, *163*, 35.
600. McNicholl, R.-A.; Lewis, F.A. The hydride phase miscibility gap in palladium-rare earth alloys. Platinum Met. Rev. **1990**, *34* (2), 81.
601. Fazle Kibria, A.K.M.; Sakamoto, Y. The effect of alloying of palladium with silver and rhodium on the hydrogen solubility, miscibility gap and hysteresis. Int. J. Hydrogen Energy **2000**, *25*, 853.
602. Fazle Kibria, A.K.M.; Sakamoto, Y. Hysteresis of pressure-composition and electrical resistance-composition isotherms of palladium–silver alloys–hydrogen system. Mater. Sci. Eng., B **1998**, *53*, 256.
603. Al-Ashab, S.T.S.; Harris, I.R. Hydrogen solubility and the equilibrium pressure-composition itotherm for Pd–Eu alloys. Int. J. Hydrogen Energy **1988**, *13* (3), 191.
604. Latyshev, V.V.; Gur'yanov, V.G. The interaction of hydrogen with palladium-based alloy membranes. Russ. J. Phys. Chem. **1988**, *62* (2), 220.
605. Cabrera, A.L.; Morales, E.; Armor, J.N. Kinetics of hydrogen desorption from palladium and ruthenium–palladium foils. J. Mater. Res. **1995**, *10* (3), 779.
606. Sakamoto, Y. Thermodynamics of solution of hydrogen in Pd–Cu and Pd–Cu–Au solid solution alloys. Ber. Bunsen-Ges. **1991**, *95* (6), 680.
607. Rodina, A.A.; Gurevich, M.A.; Doronicheva, N.I.; Mel'nikova, L.V. Interaction of hydrogen with palladium–nickel alloys. Russ. J. Phys. Chem. **1968**, *42* (4), 507.
608. Èstrin, B.M.; Roizenman, R.M. Purification of hydrogen by diffusion through a membrane made from a multicomponent palladium based alloy. J. Appl. Chem. USSR (Zh. Prikl. Khim.) **1972**, *45* (3), 667.
609. Rodina, A.A.; Gurevich, M.A.; Doronicheva, N.I. Interaction of the alloy palladium-40 wt.% silver with hydrogen. Russ. J. Phys. Chem. **1967**, *41* (9), 1286.
610. Yoshida, H.; Okuno, K.; Naruse, Y.; Kashiwai, T. Metallurgical considerations on Pd, Pd-alloy and their metal–hydrogen systems. Fusion Technol. **1985**, *8*, 2388.

611. Yasumatsu, T.; Wan, J.L.; Matsuyama, M.; Watanabe, K. Absorption of hydrogen isotopes by Pd–Pt alloys. J. Alloys Compd. **1999**, *293–295*, 900.

612. Nuovo, M.; Mazzolai, F.M.; Lewis, F.A. Studies of anelasticity in the palladium–silver–hydrogen system. J. Less-Common Met. **1976**, *49*, 37.

613. Timofeev, N.I.; Berseneva, F.N.; Makarov, V.M. New palladium-based membrane alloys for separation of gas mixtures to generate ultrapure hydrogen. Int. J. Hydrogen Energy **1994**, *19* (11), 895.

614. Kandasamy, K.; Lewis, F.A.; Sakamoto, Y.; Tong, X.Q. Hydrogen pressure and electrical resistivity dependencies on hydrogen content in the $Pd_{81}Pt_{19}H_n$ system. Int. J. Hydrogen Energy **1999**, *24*, 759.

615. Mazzolai, F.M.; Lewis, F.A. Elastic energy dissipation in the palladium–silver–hydrogen (deuterium) system. II. Zener effects. J. Phys. F: Met. Phys. **1985**, *15*, 1261.

616. Nagy, Z.; Yonco, R.M. Palladium/hydrogen membrane electrode for high temperature/high pressure aqueous solutions. J. Electrochem. Soc. **1986**, *133* (11), 2232.

617. Latyshev, V.A.; Gur'yanov, V.G.; Martynova, N.A. Dilatation of membranous alloys V-1 in hydrogen and deuterium atmospheres. Phys. Met. Metallogr. **1985**, *60* (1), 69.

618. Ryumshina, T.A.; Illyashenko, S.P. Study of stress and strain fields in an infinite plate exposed to hydrogen diffusion. Int. J. Hydrogen Energy **1999**, *24*, 825.

619. Gol'tsov, V.A.; Glukhova, Z.L.; Kotel'va, R.V. Shape change of a palladium plate upon one-side hydrogenation and subsequent degassing. Phys. Met. Metallogr. **1997**, *84* (5), 567.

620. Koshel', V.I.; Latyshev, V.V.; Gol'tsov, V.A. Thermal concentration dilation of V-2 membrane alloy in a hydrogen atmosphere. Sov. Mater. Sci. (Fiz.-Khim. Mekh. Mater.) **1984**, *20* (6), 551.

621. Latyshev, V.V. Metal diffusion membranes and hydrogen isotope separation. Soc. At. Energ. (At. Energ.) **1990**, *68* (1), 49.

622. Latyshev, V.V.; Federov, S.A. Dimensional and isotope effects of permeability of protium and deuterium in palladium membranes. Soviet Mater. Sci. (Fiz.-Khim. Mekh. Mater.) **1989**, *6*, 64.

623. Ehlers, H.; Müller, P.; Rosenstock, B. Device for the Purification of Hydrogen. US Patent 3,251,173, May 17, 1966.

624. Eguchi, T.; Goto, R. Hydrogen Purification Apparatus. US Patent 3,368, 329, Feb. 13, 1968.

625. Heuser, G. Hydrogen Diffusion Apparatus. US Patent 3,665,680, May 30, 1972.

626. Yamamoto, Y.; Goto, R. Palladium Alloy Permeable Wall for the

Separation and Purification of Hydrogen. US Patent 3,155,467, Nov. 3, 1964.

627. Nørskov, J.K.; Besenbacher, F. Theory of hydrogen interaction with metals. J. Less-Common Met. **1987**, *130*, 475.

628. Itoh, N.; Xu, W.-C.; Sathe, A.M. Capability of permeate hydrogen through palladium-based membranes for acetylene hydrogenation. Ind. Eng. Chem. Res. **1993**, *32*, 2614.

629. Fazle Kibria, A.K.M.; Sakamoto, Y. Hysteresis of pressure-composition and electrical resistance-composition isotherms of palladium–silver alloys–deuterium system. Int. J. Hydrogen Energy **1999**, *24*, 47.

630. Artman, D.; Flanagan, T.B. Diffusion of hydrogen in rhodium–palladium alloys. J. Phys. Chem. **1973**, *77* (23), 2804.

631. Tylkina, M.A.; Tsyganova, I.A. Properties of palladium–rhenium alloys. Russ. J. Inorg. Chem. (Zh. Neorg. Khim.) **1963**, *8* (10), 1229.

632. Rubin, L.R. Hydrogen Diffusion Process. US Patent 3,172,742, Mar. 9, 1965.

633. Berseneva, F.N.; Timofeev, N.I.; Makarov, V.M.; Mikhailova, I.A.; Neuimina, S.V. Effect of desorbed hydrogen on the properties of palladium–platinum alloyed with tungsten. Sov. Mater. Sci. (Fiz.-Khim. Mekh. Mater.) **1991**, *27* (6), 72.

634. Berseneva, F.N.; Zhmurko, G.P.; Neuymina, S.V.; Timofeyev, N.I. Mechanical properties and hydrogen permeability of palladium–platinum alloys modified by niobium and tantalum. Phys. Met. Metallogr. **1991**, *72* (5), 141.

635. Kurakin, V.A.; Piven, V.A.; Zakharov, A.B.; Timofeyev, N.I.; Berseneva, F.N. Volume and surface parameters of the interaction of hydrogen with palladium alloys. Phys. Met. Metallogr. **1991**, *71* (6), 127.

636. Berseneva, F.N.; Timofeev, N.I.; Zakharov, A.B. Alloys of palladium with metals of the platinum group as hydrogen-permeable membrane components at high temperatures of gas separation. Int. J. Hydrogen Energy **1993**, *18*, 15.

637. Berseneva, F.N.; Mikhailova, I.A.; Neuimina, S.V.; Timofeev, N.I. Effect of hydrogenation on the mechanical and physical properties of the alloys of palladium with molybdenum. Phys. Met. Metallogr. **1993**, *77* (1), 101.

638. Sakamoto, Y.; Chen, F.L.; Furukawa, M.; Mine, K. The ($\alpha + \beta$) hydrogen miscibility gaps in hydrogenated palladium-rich Pd–Y(Gd)–Ag ternary alloys. J. Less-Common Met. **1990**, *166*, 45.

639. Sakamoto, Y.; Chen, F.L.; Furukawa, M.; Noguchi, M. Permeability and diffusivity of hydrogen in palladium-rich Pd–Y(Gd)–Ag ternary alloys. J. Alloys Compd. **1992**, *185*, 191.

640. Tsyganova, I.A.; Roshan, N.R.; Polyakova, V.P.; Savitskiy, E.M.

Examination of the structure and properties of ternary Pd–Ru–(W, V, Ti) alloys. Russ. Metall. (Izv. Akad. Nauk SSSR, Met.) **1977** (5), 191.

641. Avertseva, I.N.; Raevskaya, M.V. Hydrogen permeability and mechanical properties of palladium alloyed with ruthenium, samarium, yttrium, and neodymium. Phys. Met. Metallogr. **1994**, *77* (5), 518.
642. Timofeyev, N.I.; Berseneva, F.N. The influence of dissolved hydrogen on the mechanical properties of alloys of palladium with rhodium. Phys. Met. Metallogr. **1991**, *72* (1), 147.
643. Goltsov, V.A.; Geld, P.V.; Kagan, G.E.; Timofeev, N.I.; Belyaev, I.F.; Mitjushov, V.A.; Kurumchina, S.K. Alloy on the Basis of Palladium for the Manufacture of Filtering Elements Used in Preparation of Hydrogen of Super-high Purity. US Patent 3,804,616, Apr. 16, 1974.
644. Berseneva, F.N.; Mikhaylova, I.A.; Timofeyev, N.I. The influence of hydrogen on the phase composition and physico-mechanical properties of the membrane palladium-based alloy V-1. Phys. Met. Metallogr. **1992**, *72* (2), 151.
645. Sarylova, M.E.; Mishchenko, A.P.; Gryaznov, V.M.; Smirnov, V.S. Effect of composition of binary palladium alloys on direction of catalytic transformations of 1,2-cyclohexanediol. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1977**, *26* (2), 389.
646. Machikina, I.Y.; Barannikova, G.A.; Gol'tsov, V.A.; Latyshev, V.V.; Kurumchina, S.K.; Timofeev, N.I. Mechanical and diffusion characteristics of palladium-base type V-3 phase-hardened alloys for hydrogen diffusion filters. Sov. Mater. Sci. (Fiz.-Khim. Mekh. Mater.) **1985**, *21* (1), 97.
647. Gol'tsov, V.A.; Latyshev, V.V.; Volkov, A.F.; Zvyagintsev, A.L.; Kuzin, A.P.; Kapyshev, V.K.; Fefelov, P.A. Diffusion filter for hydrogen isotopes. Soc. At. Energ. (At. Energ.) **1982**, *52* (2), 145.
648. Gol'tsov, V.A.; Latyshev, V.A.; Timofeev, N.I.; Machikina, I.Y. New palladium-base alloy V-2 for diffusion-type hydrogen filters. Izv. Vyssh. Uchebn. Zaved., Tsevetn. Metall. **1977** (4), 117.
649. Tebus, V.; Rivkis, L.; Arutunova, G.; Dmitrievsky, E.; Filin, V.; Golikov, Y.; Krivova, V.; Kapychev, V. Investigation of palladium alloy properties degradation during long-time tritium exposure. J. Nucl. Mater. **1999**, *271–272*, 345.
650. Latyshev, V.V.; Gol'tsov, V.A.; Federov, S.A. Separation of hydrogen isotopes by metal membranes. Soc. At. Energ. (At. Energ.) **1982**, *53* (1), 482.
651. Skorodumov, B.G.; Ulanov, V.G.; Zhukovskaya, E.V.; Zhukovskii, O.A. Investigation of stationary and diffusional concentration profiles of hydrogen isotopes in nuclear materials by the Neutron Elastic Recoil Detection (NERD) method. Phys. Met. Metallogr. **1997**, *83* (1), 61.

652. Goltsov, V.A.; Timofeev, N.I.; Guschin, S.G. Palladium-based Alloy. US Patent 4,063,937, Dec. 20, 1977.

653. Cornell, D.A.; Seymour, E.F.W. Nuclear magnetic resonance study of hydrogen diffusion in palladium and palladium–cerium alloys. J. Less-Common Met. **1975**, *39*, 43.

654. Ramaprabhu, S. Thermodynamics and stability of dissolved hydrogen in Pd rich binary $Pd_{1-x}Z_x$ and ternary $Pd_{1-x-y}Z_xZ_y$' solid solution alloys. Int. J. Hydrogen Energy **1998**, *23* (9), 787.

655. Weiss, A.; Ramaprabhu, S.; Rajalakshmi, N. Hydrogen solubility and thermodynamics of hydrogen absorption in palladium-rich binary $Pd_{1-x}Z_x$ and ternary $Pd_{1-x-y}Z_xZ_y$' solid solution alloys. Z. Phys. Chem. N.F. **1997**, *199*, 165.

656. Yoshinari, O.; Matsuda, H.; Fukuhara, K.; Tanaka, K. Hydrogen diffusivity and solubility in Pd–Y alloys. Mater. Trans., JIM **1997**, *38* (6), 508.

657. Sakamoto, Y.; Chen, F.L.; Kinari, Y. Permeability and diffusivity of hydrogen through Pd–Y–In(Sn, Pb) alloy membranes. J. Alloys Compd. **1994**, *205*, 205.

658. Sakamoto, Y.; Ishimaru, N.; Inoue, Y. Solubility of hydrogen in palladium–yttrium–silver alloys. Ber. Bunsen-Ges. **1992**, *96* (2), 128.

659. Lewis, F.A.; Kandasamy, K.; McNicholl, R.-A.; Tong, X.Q. Hydrogen pressure-hydrogen content and electrical resistance-hydrogen content relationships of palladium and palladium alloy–hydrogen systems. Int. J. Hydrogen Energy **1995**, *20* (5), 369.

660. Yoshihara, M.; McLellan, R.B. Palladium–cerium–hydrogen solid solutions—I. Thermodynamic properties. Acta Metall. Mater. **1988**, *36* (12), 3217.

661. Yoshihara, M.; McLellan, R.B. Palladium–cerium–hydrogen solid solutions—II. Kinetic properties. Acta Metall. Mater. **1988**, *36* (12), 3225.

662. Yoshihara, M.; McLellan, R.B. The thermodynamics of hydrogen in palladium–yttrium solid solutions. Acta Metall. Mater. **1988**, *36* (2), 385.

663. Hughes, D.T.; Harris, I.R. A comparative study of hydrogen permeabilities and solubilities in some palladium solid solution alloys. J. Less-Common Met. **1978**, *61*, 9.

664. Hughes, D.T.; Harris, I.R. Hydrogen diffusion membranes based on some palladium-rare earth solid solution alloys. Z. Phys. Chem. N.F. **1979**, *117*, 185.

665. Doyle, M.L.; Harris, I.R. Palladium-rare earth alloys. Platinum Met. Rev. **1988**, *32* (3), 130.

666. Chen, F.L. Hydrogen solubility in palladium–ytterbium solid solution alloys. J. Less-Common Met. **1991**, *172–174*, 56.

667. Kandasamy, K.; Lewis, F.A.; McFall, W.D.; McNicholl, R.-A. Atomic dimensional influences on patterns of p-c(n)-T and other relationships of palladium alloy–hydrogen systems. Z. Phys. Chem. N.F. **1989**, *163*, 41.
668. McNicholl, R.-A.; Lewis, F.A. Some features of $p$–$n$ and $R/R_0$–$n$ relationships of hydrogen systems of Pd alloys with metals in groups 3, 4 and 5. Z. Phys. Chem. N.F. **1993**, *181*, 239.
669. Farr, J.P.G.; Harris, I.R. Hydrogen Diffusion Membranes. US Patent 3, 713,270, Jan. 30, 1973.
670. Fromageau, R.; Magnouche, A. Solubility and Diffusion of Hydrogen in the Amorphous Alloy $Pd_{80}Si_{20}$. Z. Phys. Chem. N.F. **1985**, *145*, 523.
671. Astakhov, I.I.; Kazarinov, V.E.; Reznikova, L.A.; Teplitskaya, G.L. Diffusion of hydrogen isotopes in palladium hydride and deuteride in the presence of lithium. Russ. J. Electrochem. (Elektrokhimiya) **1994**, *30* (12), 1507.
672. Allard, K.D.; Flanagan, T.B. The diffusion of hydrogen in boron–palladium alloys. J. Phys. Chem. **1970**, *74* (2), 298.
673. McKinley, D.L. Metal Alloy for Hydrogen Separation and Purification. US Patent 3,350,845, Nov. 7, 1967.
674. Edlund, D.J. Composite Hydrogen Separation Element and Module. EP Patent 783919, 1997.
675. Knapton, A.G. Palladium alloys for hydrogen diffusion membranes: A review of high permeability materials. Platinum Met. Rev. **1977**, *21* (2), 44.
676. Piper, J. Diffusion of hydrogen in copper–palladium alloys. J. Appl. Phys. **1966**, *37* (2), 715.
677. Mishchenko, A.P.; Sarylova, M.E.; Gryaznov, V.M.; Smirnov, V.S.; Roshan, N.R.; Polyakova, V.P.; Savitskii, E.M. Hydrogen permeability and catalytic activity of membranes made from palladium–copper alloys in the dehydrogenation of 1,2-cyclohexanediol. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1977**, *7*, 1490.
678. McKinley, D.L. Method for Hydrogen Separation and Purification. US Patent 3,439,474, Apr. 22, 1969.
679. Karpova, R.A.; Tverdovskii, I.P. Sorption of hydrogen by disperse palladium–copper alloys. Russ. J. Phys. Chem. **1959**, *33* (6), 1393.
680. Flanagan, T.B.; Chisdes, D.M. Solubility of hydrogen (1 atm, 298 K) in some copper/palladium alloys. Solid State Commun. **1975**, *16* (5), 529.
681. Fisher, D.; Chisdes, D.M.; Flanagan, T.B. Solution of hydrogen in palladium/copper alloys. J. Solid State Chem. **1977**, *20*, 149.
682. Zetkin, A.S.; Kagan, G.E.; Varaksin, A.N.; Levin, E.S. Diffusion and penetrability of deuterium in the alloy Pd-53 at.% Cu. Sov. Phys. Solid State (Fiz. Tverd. Tela) **1992**, *34* (1), 83.

683. Zetkin, A.S.; Kagan, G.Y.; Levin, Y.S. Influence of structural transformations on the diffusion parameters of deuterium in palladium–copper alloys. Phys. Met. Metallogr. **1987**, *64* (5), 130.
684. Alefeld, G. Metal hydrides in energy conversion systems. Trans., JIM (Proceedings of JIMIS—2. Hydrogen in Metals) **1980**, *21* (Supplement), 25.
685. Johansson, C.H.; Linde, J.O. 3. Röntgenographische Bestimmung der Atomanordnung in den Mischkristallreihen Au–Cu und Pd–Cu. Ann. Phys. **1925**, *78*, 439.
686. Vert, Z.L.; Drozdova, N.V. Solubility of hydrogen in alloys of the palladium–copper system. J. Appl. Chem. USSR (Zh. Prikl. Khim.) **1990**, *63* (11), 2365.
687. Vert, Z.L.; Mosevich, I.A.; Tverdovskii, I.P. X-ray study of the solubility of hydrogen in finely divided and in massive palladium. Russ. J. Phys. Chem. **1965**, *39* (5), 566.
688. Lianos, L.; Debauge, J.; Jugnet, Y.; Bertolini, J.C. 1,3-butadiene hydrogenation on $Pd_{50}Cu_{50}$ single crystals. Catal. Lett. **1997**, *44*, 211.
689. Tosti, S.; Violante, V.; Basile, A.; Chiappetta, G.; Castelli, S.; De Francesco, M.; Scaglione, S.; Sarto, F. Catalytic membrane reactors for tritium recovery from tritiated water in the ITER fuel cycle. Fusion Eng. Des. **2000**, *49–50* (953-8).
690. Tosti, S.; Bettinali, L.; Violante, V. Rolled thin Pd and Pd–Ag membranes for hydrogen separation and production. Int. J. Hydrogen Energy **2000**, *25* (4), 319.
691. Gryaznov, V.M.; Maganyuk, A.P.; Gizhevskii, S.F.; Mardilovich, I.P. New methods for liquid hydrogenation on supported metal catalysts. Dokl. Phys. Chem. **1998**, *362* (6), 350.
692. Adris, A.M.; Lim, C.J.; Grace, J.R. The fluidized bed membrane reactor system: A pilot scale experimental study. Chem. Eng. Sci. **1994**, *49* (24B), 5833.
693. Dobo, E.J.; Graham, T.E. Inorganic Anisotropic Hollow Fibers. US Patent 4,329,157, May 11, 1982.
694. Wachtman, J.B., Jr.; Haber, R.A. New technology in the CPI: Ceramic films and coatings. Chem. Eng. Prog. **1986**, *82* (1), 39.
695. Basile, A.; Drioli, E.; Santella, F.; Violante, V.; Capannelli, G.; Vitulli, G. A study on catalytic membrane reactors for water gas shift reaction. Gas Sep. Purif. **1996**, *10* (1), 53.
696. Mattox, D.M. Physical vapor deposition (PVD) processes. Met. Finish. **1999**, *97* (1), 417.
697. Greene, J.E. Chapter 13. In *Handbook of Deposition Technologies for Films and Coatings*; Bunshah, R.F., Ed.; Noyes Publications: Park Ridge, New Jersey, US, 1982.

698. Thornton, J.A. High rate thick film growth. Annu. Rev. Mater. Sci. **1977**, *7*, 239.
699. Machlin, E.S. *Materials Science in Microelectronics*; GIRO PRESS: Croton-on-Hudson, NY, 1995.
700. Gillet, E.; El Yakhloufi, M.H.; Disalvo, J.-P.; Abdelouahab, F.B. In situ characterization of ultra-thin palladium deposits on $\alpha$- and $\gamma$-alumina. Surf. Sci. **1999**, *419*, 216.
701. Reichelt, K.; Jiang, X. The preparation of thin films by physical vapour deposition methods. Thin Solid Films **1990**, *191*, 91.
702. Murr, L.E. Effects of substrate temperature, pressure, and high evaporation rates on nucleation, epitaxy, and structure of palladium thin films. Thin Solid Films **1971**, *7*, 101.
703. McCool, B.; Xomeritakis, G.; Lin, Y.S. Composition control and hydrogen permeation characteristics of sputter deposited palladium–silver membranes. J. Membr. Sci. **1999**, *161*, 67.
704. Thomann, A.-L.; Rozenbaum, J.P.; Brault, P.; Andreazza-Vignole, C.; Andreazza, P. Pd nanoclusters grown by plasma sputtering deposition on amorphous substrates. Appl. Surf. Sci. **2000**, *158*, 172.
705. Marshall, I.J. Method and Apparatus for Linear Magnetron Sputtering. US Patent 5,298,137, Mar. 29, 1994.
706. Feurer, E.; Suhr, H. Thin palladium films prepared by metal-organic plasma-enhanced chemical vapour deposition. Thin Solid Films **1988**, *157*, 81.
707. Atanosova, P.; Bhaskaran, V.; Kodas, T.; Smith, H.M. Oxidation resistance of copper alloy thin films formed by chemical vapor deposition. Mater. Res. Soc. Symp. Proc. **1996**, *428*, 25.
708. Morooka, S.; Yan, S.; Yokoyama, S.; Kusakabe, K. Palladium membrane formed in macropores of support tube by chemical vapor deposition with crossflow through a porous wall. Sep. Sci. Technol. **1995**, *30* (14), 2877.
709. Gazula, R.; Ward, T.L. *Controlled Deposition and Infiltration of Pd in Porous Substrates by MOCVD*. Conference proceedings, AIChE Annual Mtg., Los Angeles, California, Nov. 16–21, 1997.
710. Xomeritakis, G.; Lin, Y.S. Fabrication of a thin palladium membrane supported in a porous ceramic substrate by chemical vapor deposition. J. Membr. Sci. **1996**, *120*, 261.
711. Gräfe, A.; Heinen, R.; Klein, F.; Kruck, T.; Scherer, M.; Schober, M. Precursor development for the chemical vapor deposition of aluminium, copper and palladium. Appl. Surf. Sci. **1995**, *91*, 187.
712. Natter, H. Nanocrystalline palladium by pulsed electrodeposition. Ber. Bunsen-Ges. **1996**, *100* (1), 55.
713. Bryden, K.J.; Ying, J.Y. Electrodeposition synthesis and hydrogen

absorption properties of nanostructured palladium–iron alloys. Nanostruct. Mater. **1997**, *9*, 485.

714. Bryden, K.J.; Ying, J.Y. Pulsed electrodeposition synthesis and hydrogen absorption properties of nanostructured palladium–iron alloy films. J. Electrochem. Soc. **1998**, *145* (10), 3339.
715. Shu, J.; Grandjean, B.P.A.; Kaliaguine, S. Autocatalytic effects in electroless deposition of palladium. J. Electrochem. Soc. **1993**, *140* (11), 3175.
716. Saubestre, E.B. Electroless plating today. Met. Finish. **1962**, *60* (6), 67.
717. Saubestre, E.B. Electroless plating today. Met. Finish. **1962**, *60* (7), 49.
718. Saubestre, E.B. Electroless plating today. Met. Finish. **1962**, *60* (8), 45.
719. Saubestre, E.B. Electroless plating today. Met. Finish. **1962**, *60* (9), 59.
720. Mallory, G.O.; Hajdu, J.B. *Electroless Plating*; American Electroplaters and Surface Finishers Society: Orlando, Florida, 1990.
721. Lukes, R.M. The chemistry of the autocatalytic reduction of copper by alkaline formaldehyde. Plating **1964**, *51*, 1066.
722. Iacovangelo, C.D. Autocatalytic electroless gold deposition using hydrazine and dimethylamine borane as reducing agents. J. Electrochem. Soc. **1991**, *138* (4), 976.
723. Horkans, J. A cyclic voltammetric study of Pd–Sn colloidal catalysts for electroless deposition. J. Electrochem. Soc. **1983**, *130* (2), 311.
724. Dubin, V.; Shacham-Diamond, Y. Selective and blanket electroless copper deposition for ultralarge scale integration. J. Electrochem. Soc. **1997**, *144* (3), 898.
725. Nakahara, S.; Mak, C.Y.; Okinaka, Y. Effect of the type of substrates on the ductility and microstructure of electroless copper deposits. J. Electrochem. Soc. **1993**, *140* (2), 533.
726. Ameen, J.G.; McBride, D.G.; Phillips, G.C. Etching of high alumina ceramics to promote copper adhesion. J. Electrochem. Soc. **1973**, *120* (11), 1518.
727. Elmore, G.V.; Hershberger, R.F. Molten alkali treatment of alumina surfaces for bonding to electroless copper. J. Electrochem. Soc. **1974**, *121* (1), 107.
728. Iacovangelo, C.D.; Jerabek, E.C.; King, R.N. Ceramic metallization using molten salt and electroless plating. Plat. Surf. Finish. **1994**, *81* (1), 54.
729. De Graef, M.; Dalgleish, B.J.; Turner, M.R.; Evans, A.G. Interfaces between alumina and platinum: structure, bonding and fracture resistance. Acta Metall. Mater. **1992**, *40*, S333.
730. Marturano, M.A.; Aglietti, E.F.; Ferretti, O.A. Preparation and characterization of $\alpha$-$Al_2O_3$ catalytic supports. Application to methane steam reforming. Ann. Chim. Sci. Mater. **1997**, *22*, 53.

731. Honma, H.; Kanemitsu, K. Electroless nickel plating on alumina ceramics. Plat. Surf. Finish. **1987**, *74* (9), 62.
732. Ocken, H.; Lin, C.C.; Lister, D.H. Thin films to impede the incorporation of radionuclides in austenitic stainless steels. Thin Solid Films **1989**, *171* (2), 323.
733. Ocken, H.; Pound, B.G.; Lister, D.H. Deposition and characterization of electroless palladium on austenitic stainless steel. Thin Solid Films **1989**, *171*, 313.
734. Shu, J.; Grandjean, B.P.A.; Ghali, E.; Kaliaguine, S. Simultaneous deposition of Pd and Ag on porous stainless steel by electroless plating. J. Membr. Sci. **1993**, *77*, 181.
735. Buxbaum, R.E. Composite Metal Membrane for Hydrogen Extraction. US Patent 5,215,729, 1993.
736. Buxbaum, R.E.; Hsu, P.C. Method for Plating Palladium. US Patent 5,149,420, Sep. 22, 1992.
737. Mardilovich, P.P.; Kurman, P.V.; Govyadinov, A.N.; Mardilovich, I.P.; Paterson, R.; Gryaznov, V.M. Gas permeability of anodized alumina membranes with a palladium–ruthenium alloy layer. Russ. J. Phys. Chem. **1996**, *70* (3), 514.
738. Abys, J.A.; Straschil, H.K. Acidic Palladium Strike Bath. EP Patent 512724, 1995.
739. Straschil, H.K.; Abys, J.A.; Kudrak, E.J.; Maisano, J.J.; Nakahara, S. New palladium strike improves adhesion and porosity. Met. Finish. **1992**, *90* (1), 42.
740. Leibowitz, G.; Mullaney, R.L. Electroless Nickel Plating. US Patent 3,597,266, Aug. 3, 1971.
741. Rhoda, R.N. Electroless plating with precious metals. Plating **1963**, *50*, 307.
742. Rhoda, R.N. Barrel plating by means of electroless palladium. J. Electrochem. Soc. **1961**, *108*, 707.
743. Rhoda, R.N. Electroless palladium plating. Trans. Inst. Met. Finish. **1959**, *36*, 82.
744. Ohno, I. Electrochemistry of electroless plating. Mater. Sci. Eng. **1991**, *A146*, 33.
745. Rothschild, B.F.; Nabors, R.G. Quantitative adhesion measurements of electroless copper to copper and gold. Plating **1964**, *51* (11), 1063.
746. Lea, C.; Whitlaw, K.J. The importance of electrokinetic potential in the catalysis of electroless copper on epoxy-glassfibre laminates. Trans. Inst. Met. Finish. **1986**, *64*, 124.
747. Baylis, B.K.W.; Huang, C.-C.; Schlesinger, M. A study of the products of ultraviolet irradiation of palladium-containing catalysts for electroless metal deposition. J. Electrochem. Soc. **1979**, *126* (3), 394.

748. Besenhard, J.O.; Krebber, U.; Hörber, J.K.H.; Kanani, N.; Meyer, H. A STM study of Pd-catalyst for electroless Cu deposition on nonconductors by means of a modified graphite substrate. J. Electrochem. Soc. **1989**, *136* (12), 3608.
749. Charbonnier, M.; Romand, M.; Harry, E.; Alami, M. Surface plasma functionalization of polycarbonate: Application to electroless nickel and copper plating. J. Appl. Electrochem. **2001**, *31*, 57.
750. Charbonnier, M.; Alami, M.; Romand, M. Plasma treatment process for palladium chemisorption onto polymers before electroless deposition. J. Electrochem. Soc. **1996**, *143* (2), 472.
751. Cohen, R.L.; Meek, R.L. The chemistry of palladium–tin colloid sensitizing processes. J. Colloid Interface Sci. **1976**, *55* (1), 156.
752. de Minjer, C.H.; v.d. Boom, P.F.J. The nucleation with $SnCl_2$–$PdCl_2$ solutions of glass before electroless plating. J. Electrochem. Soc. **1973**, *120* (12), 1644.
753. Dressick, W.J.; Kondracki, L.M.; Chen, M.-S.; Brandow, S.L.; Matijevic, E.; Calvert, J.M. Characterization of a colloidal Pd(II)-based catalyst dispersion for electroless metal deposition. Colloids Surf., A **1996**, *108* (1), 101.
754. Feldstein, N.; Weiner, J.A. Surface characterization of sensitized and activated teflon. J. Electrochem. Soc. **1973**, *120* (4), 475.
755. Feldstein, N.; Weiner, J.A.; Schnable, G.L. Some aspects of the chemistry of tin sensitizing solutions. J. Electrochem. Soc. **1972**, *119* (11), 1486.
756. Feldstein, N.; Weiner, J.A.T. The effectiveness of tin sensitizer solutions. Plat. Surf. Finish. **1972**, *59* (2), 140.
757. Flis, J.; Duquette, D.J. Initiation of electroless nickel plating on copper, palladium-activated copper, gold, and platinum. J. Electrochem. Soc. **1984**, *131* (2), 254.
758. Froment, M.; Queau, E.; Martin, J.R.; Stremsdoerfer, G. Structural and analytical characteristics of adsorbed Pd–Sn colloids. J. Electrochem. Soc. **1995**, *142* (10), 3373.
759. Fujinami, T.; Watanabe, J.; Honma, H. Catalytic activity and stability of mixed $PdCl_2/SnCl_2$ catalysts. Trans. Inst. Met. Finish. **1996**, *74* (6), 193.
760. Grunwald, J.J.; Gottesfeld, S.; Laser, D. An Auger spectroscopic study of the catalysis process for electroless copper plating. Plat. Surf. Finish. **1981**, *68* (10), 71.
761. Horkans, J. Comparison of the activity of PdSn colloidal catalysts with the activity of pure metals for HCHO oxidation: Enhancement of the activity by ionic tin. J. Electrochem. Soc. **1984**, *131* (8), 1853.
762. Horkans, J.; Sambucetti, C.; Markovich, V. Initiation of electroless Cu plating on nonmetallic surfaces. IBM J. Res. Dev. **1984**, *28* (6), 690.

763. Lafferty, E.J.; Macauley, D.J.; Kelly, P.V.; Crean, G.M. Atomic force microscopy investigation of the morphology of a UV photodefined palladium activation layer on alumina ceramic and the nucleation of electroless copper at the activated sites. Mater. Res. Soc. Symp. Proc. **1997**, *441*, 329.

764. Matijevic', E.; Poskanzer, A.M.; Zuman, P. The characterization of the stannous chloride/palladium chloride catalysts for electroless plating. Plat. Surf. Finish. **1975**, *62* (10), 958.

765. Meek, R.L. A Rutherford scattering study of catalyst systems for electroless Cu plating. J. Electrochem. Soc. **1975**, *122* (9), 1177.

766. Meek, R.L. A Rutherford scattering study of catalyst systems for electroless Cu plating. J. Electrochem. Soc. **1975**, *122* (11), 1478.

767. Osaka, T.; Nagasaka, H. An electron diffraction study on mixed $PdCl_2$/$SnCl_2$ catalysts for electroless plating. J. Electrochem. Soc **1980**, *127* (11), 2343.

768. Osaka, T.; Nagasaka, H. Effects of activation and acceleration on magnetic properties of chemically deposited Co–P thin films. J. Electrochem. Soc. **1981**, *128* (8), 1686.

769. Osaka, T.; Takematsu, H.; Nihei, K. A study on activation and acceleration by mixed $PdCl_2$/$SnCl_2$ catalysts for electroless metal deposition. J. Electrochem. Soc. **1980**, *127* (5), 1021.

770. Pearlstein, F. Electroless nickel deposition: Activation of non-metallic surfaces. Met. Finish. **1955**, *53* (8), 59.

771. Pederson, L.R. Comparison of stannous and stannic chloride as sensitizing agents in the electroless deposition of silver on glass using x-ray photoelectron spectroscopy. Sol. Energy Mater. **1982**, *6*, 221.

772. Rantell, A.; Holtzman, A. Mechanism of activation of polymer surfaces by mixed stannous chloride/palladium chloride catalysts. Trans. Inst. Met. Finish. **1973**, *51*, 62.

773. Rantell, A.; Holtzman, A. Mixed stannous chloride–palladium chloride activators: A study of their formation and nature. Plating **1974**, *61* (4), 326.

774. Schlesinger, M.; Kisel, J. Effect of Sn(II)-based sensitizer adsorption in electroless deposition. J. Electrochem. Soc. **1989**, *136* (6), 1658.

775. Siperko, L.M. Scanning tunneling microscopy studies of Pd–Sn catalyzed electroless Cu deposited on pyrolytic graphite. J. Vac. Sci. Technol., A **1991**, *9* (3), 1457.

776. Wang, Y.H.; Wan, C.C. The kinetics of $PdCl_2$/$SnCl_2$ activating solutions for electroless plating. Plat. Surf. Finish. **1982**, *69* (8), 59.

777. Shafeev, G.A.; Themlin, J.-M.; Bellard, L.; Marine, W.; Cros, A. Enhanced adherence of area-selective electroless metal plating on insulators. J. Vac. Sci. Technol., A **1996**, *14* (2), 319.

778. Sricharoenchaikit, P. Thin metal film formation using electroless plating. J. Electrochem. Soc. **1993**, *140* (7), 1917.
779. Keuler, J.N.; Lorenzen, L.; Sanderson, R.N.; Linkov, V. Optimizing palladium conversion in electroless palladium plating of alumina membranes. Plat. Surf. Finish. **1997**, *84* (8), 34.
780. Norsworthy, B.E. The theory and practice of electroless copper deposition and use of electroless plating in the electronics industry. Trans. Inst. Met. Finish. **1977**, *55*, 31.
781. Hulteen, J.C.; Martin, C.R. A general template-based method for the preparation of nanomaterials. J. Mater. Chem. **1997**, *7* (7), 1075.
782. Hulteen, J.C.; Menon, V.P.; Martin, C.R. Template preparation of nanoelectrode ensembles. J. Chem. Soc., Faraday Trans. **1996**, *92* (20), 4029.
783. Menon, V.P.; Martin, C.R. Fabrication and evaluation of nanoelectrode ensembles. Anal. Chem. **1995**, *67* (13), 1920.
784. Cohen, R.L.; West, K.W. Solution chemistry and colloid formation in the tin chloride sensitizing process. J. Electrochem. Soc. **1972**, *119* (4), 433.
785. Sard, R. The nucleation, growth, and structure of electroless copper deposits. J. Electrochem. Soc. **1970**, *117* (7), 864.
786. D'Amico, J.F.; De Angelo, M.A.; Henrickson, J.F.; Kenney, J.T.; Sharp, D.J. Selective elec1troless metal deposition using patterned photo-oxidation of Sn(II) sensitized substrates. J. Electrochem. Soc. **1971**, *118* (10), 1695.
787. Kim, J.; Wen, S.H.; Jung, D.Y.; Johnson, R.W. Microstructure evolution during electroless copper deposition. IBM J. Res. Dev. **1984**, *28* (6), 697.
788. Biswas, D.R. Review: Deposition processes for films and coatings. J. Mater. Sci. **1986**, *21*, 2217.
789. Deng, H.; Moller, P. Effect of the substrate surface morphology on the porosity of electroless nickel coatings. Trans. Inst. Met. Finish. **1993**, *71* (4), 142.
790. Uzio, D.; Peureux, J.; Fendler, A.; Giroir-Ramsay, J.; Dalmon, J. A platinum/$\gamma-Al_2O_3$–catalytic membrane: Preparation, morphological and catalytic characterizations. Appl. Catal., A **1993**, *96* (1), 83.
791. Lambert, C.K.; Gonzalez, R.D. Activity and selectivity of a Pd/$\gamma-Al_2O_3$ catalytic membrane in the partial hydrogenation reactions of acetylene and 1,3-butadiene. Catal. Lett. **1999**, *57*, 1.
792. Li, A.; Xiong, G.; Gu, J.; Zheng, L. Preparation of Pd/ceramic composite membrane 1. Improvement of the conventional preparation technique. J. Membr. Sci. **1996**, *110*, 257.
793. Gross, M.E.; Appelbaum, A.; Gallagher, P.K. Laser direct-write metallization in thin palladium acetate films. J. Appl. Phys. **1987**, *61* (4), 1628.

794. Schrott, A.G.; Braren, B.; Saraf, R. Laser assisted Pd seeding for electroless plating on $SiO_2$. Appl. Phys. Lett. **1994**, *64* (12), 1582.
795. Zhang, J.-Y.; Boyd, I.W.; Esrom, H. Lamp-induced forward transfer: A new approach for deposition of metal films. J. Mater. Sci. Lett. **1998**, *17*, 2037.
796. Zhang, J.-Y.; Boyd, I.W. Investigations of photo-induced decomposition of palladium acetate for electroless copper plating. Thin Solid Films **1998**, *318* (1–2), 234.
797. Sun, Y.-M.; Khang, S.-J. Catalytic membrane for simultaneous chemical reaction and separation applied to a dehydrogenation reaction. Ind. Eng. Chem. Res. **1988**, *27* (7), 1136.
798. Sun, Y.-M.; Khang, S.-J. A catalytic membrane reactor: Its performance in comparison with other types of reactors. Ind. Eng. Chem. Res. **1990**, *29*, 232.
799. Wu, L.-Q.; Xu, N.; Shi, J. Novel method for preparing palladium membranes by photocatalytic deposition. AIChE J. **2000**, *46* (5), 1075.
800. Shu, J.; Grandjean, B.P.A.; Kaliaguine, S. Morphological study of hydrogen permeable Pd membranes. Thin Solid Films **1994**, *252* (1), 26.
801. Shu, J.; Adnot, A.; Grandjean, B.P.A.; Kaliaguine, S. Structurally stable composite Pd–Ag alloy membranes: Introduction of a diffusion barrier. Thin Solid Films **1996**, *286* (1–2), 72.
802. Shu, J.; Grandjean, B.P.A.; Kaliaguine, S. Methane steam reforming in asymmetric Pd– and Pd–Ag/porous SS membrane reactors. Appl. Catal., A **1994**, *119*, 305.
803. Souleimanova, R.S.; Mukasyan, A.S.; Varma, A. Study of structure formation during electroless plating of thin metal-composite membranes. Chem. Eng. Sci. **1999**, *54*, 3369.
804. Souleimanova, R.S.; Mukasyan, A.S.; Varma, A. Effects of osmosis on microstructure of Pd-composite membranes synthesized by electroless plating technique. J. Membr. Sci. **2000**, *166*, 249.
805. Yeung, K.L.; Varma, A. Novel preparation techniques for thin metal–ceramic composite membranes. AIChE J. **1995**, *41* (9), 2131.
806. Yeung, K.L.; Sebastian, J.M.; Varma, A. Novel preparation of Pd/Vycor composite membranes. Catal. Today **1995**, *25* (3–4), 231.
807. Yeung, K.L.; Aravind, R.; Zawada, R.J.X.; Szegner, J.; Cao, G.; Varma, A. Nonuniform catalyst distribution for inorganic membrane reactors: Theoretical considerations and preparation techniques. Chem. Eng. Sci. **1994**, *49* (24A), 4823.
808. Zheng, W.; Wu, L.-Q. Preparation and pore size shrinkage of palladium–ceramic composite membrane by electroless plating under hydrothermal conditions. Mater. Sci. Eng., A **2000**, *283*, 122.

809. Takahashi, T.; Kosaka, S. Gas Separator and Method for Preparing It. US Patent 5,980,989, Nov. 9, 1999.
810. Kosaka, S.; Sakai, O.; Takahashi, T.; Soma, T. Hydrogen Separator, Hydrogen Separating Apparatus and Method for Manufacturing Hydrogen Separator. US Patent 5,614,001, Mar. 25, 1997.
811. Bindra, P.; Tweedie, J. Mechanisms of electroless metal plating: I. Application of the mixed potential theory. J. Electrochem. Soc. **1983**, *130* (5), 1112.
812. Chou, M.L.; Manning, N.; Chen, H. Deposition and characterization of thin electroless palladium films from newly developed baths. Thin Solid Films **1992**, *213*, 64.
813. Schumacher, R.; Pesek, J.J.; Melroy, O.R. Kinetic analysis of electroless deposition of copper. J. Phys. Chem. **1985**, *89*, 4338.
814. Bindra, P.; Light, D.; Rath, D. Mechanisms of electroless metal plating: I. Mixed potential theory and the interdependence of partial reactions. IBM J. Res. Dev. **1984**, *28* (6), 668.
815. Athavale, S.N.; Totlani, M.K. Electroless plating of palladium. Met. Finish. **1989**, *87*, 23.
816. Bindra, P.; Roldan, J.M.; Arbach, G.V. Mechanisms of electroless metal plating: II. Decomposition of formaldehyde. IBM J. Res. Dev. **1984**, *28* (6), 679.
817. Cheng, Y.S.; Yeung, K.L. Effects of electroless plating chemistry on the synthesis of palladium membranes. J. Membr. Sci. **2001**, *182*, 195.
818. Cheng, Y.S.; Yeung, K.L. Palladium–silver composite membranes by electroless plating technique. J. Membr. Sci. **1999**, *158* (1–2), 127.
819. Zhao, H.-B.; Pflanz, K.; Gu, J.-H.; Li, A.-W.; Stroh, N.; Brunner, H.; Xiong, G.-X. Preparation of palladium composite membranes by modified electroless plating procedure. J. Membr. Sci. **1998**, *142*, 147.
820. Chou, M.L.; Chen, H. The influence of boric acid and dissolved oxygen on the morphology of electroless palladium films. Thin Solid Films **1992**, *208* (2), 210.
821. Steinmetz, P.; Alperine, S.; Friant-Costantini, A.; Josso, P. Electroless deposition of pure nickel, palladium and platinum. Surf. Coat. Technol. **1990**, *43/44* (1–3), 500.
822. Govind, R.; Atnoor, D. Development of a composite palladium membrane for selective hydrogen separation at high temperature. Ind. Eng. Chem. Res. **1991**, *30* (3), 591.
823. Mallory, G.O.; Baudrand, D.W. Bath and Process for Chemical Metal Plating. US Patent 3,597,267, Aug. 3, 1971.
824. Vaiman, L.A. Apparatus and Method for Extracting Hydrogen. US Patent 5,205,841, Apr. 27, 1993.
825. Low, G.M.; Albright, C.F. Process for Separation of Dissolved

Hydrogen from Water by Use of Palladium and Process for Coating Palladium with Palladium Black. US Patent 3,678,654, Jul. 25, 1972.

826. Shirogami, T.; Murata, K. Cathodic $H_2$ gas production through Pd alloy membrane electrodes. Int. J. Hydrogen Energy **1982**, *7* (11), 877.

827. Sokol'skii, D.V.; Nogerbekov, B.Y.; Gudeleva, N.N.; Kobets, N.V. Hydrogen adsorption at palladium membranes. Sov. Electrochem. (Elektrokhimiya) **1988**, *24* (7), 919.

828. Skorodumov, B.G.; Yatsevich, I.O.; Zhukovsky, O.A. Investigation of hydrogen isotope behaviour in palladium membrane cathodes in the process of water electrolysis by the NERD method. Nucl. Instrum. Methods Phys. Res., Sect. B **1994**, *85*, 301.

829. Wynblatt, P.; Gjostein, N.A. Particle growth in model supported metal catalysts—I. Theory. Acta Metall. Mater. **1976**, *24*, 1165.

830. Wynblatt, P. Particle growth in model supported metal catalysts—II. Comparison of experiment with theory. Acta Metall. Mater. **1976**, *24*, 1175.

831. Matsuoka, M.; Yoshida, Y.; Iwakura, C. The effects of aeration and accumulation of carbonate ions on the mechanical properties of electroless copper coatings. J. Electrochem. Soc. **1995**, *142* (1), 87.

832. Molenaar, A.; Holdrinet, F.E.; van Beek, L.K.H. Kinetics of electroless copper plating with EDTA as the complexing agent for cupric ions. Plating **1974**, *61* (3), 238.

833. Bindra, P.; Roldan, J. Mechanisms of electroless metal plating II. Formaldehyde oxidation. J. Electrochem. Soc. **1985**, *132* (11), 2581.

834. Uemiya, S.; Katoh, W.; Niizato, T.; Hatakeyama, N.; Kojima, T.; Mizumoto, K.; Doi, T. In *Supported Palladium and Silver Alloy Membrane for Hydrogen Separation Prepared by Electroplating Technique*, 6th Intl. Conf. Inorganic Membranes, Montpellier, France, June 26–30, 2000; P205.

835. Yu, G.; Li, L.; Yang, N. In *Preparation of Pd–Ag Alloy Composite Membrane by Electroless Codeposition Plating*, Proc. 5th Intl. Conf. Inorganic Membr., Nagoya, Japan, June 22–26, 1998; 74.

836. Sturzenegger, B.; Puippe, J.C. Electrodeposition of palladium–silver alloys from ammoniacal electrolytes. Platinum Met. Rev. **1984**, *20*, 117.

837. Belser, R.B. Alloying behavior of thin bimetal films, simultaneously or successively deposited. J. Appl. Phys. **1960**, *31* (3), 562.

838. Bitler, W.R.; Pickering, H.W.; Kaja, S. Interdiffusion kinetics of copper with palladium. Plat. Surf. Finish. **1985**, *72* (12), 60.

839. Bukaluk, A. AES studies of interdiffusion in thin copper–palladium multilayer structures. Vacuum **1999**, *54*, 279.

840. Langley, R.C.; Myers, M.; Myers, H. Method for Producing Hydrogen Diffusion Cells. US Patent 3,428,476, Feb. 18, 1969.

841. Sanders, A.P. Endothermal Water Decomposition Unit for Producing Hydrogen and Oxygen. US Patent 4,254,086, Mar. 3, 1981.

842. Xu, Z.R.; McLellan, R.B. Hydrogen enhanced diffusional creep. Acta Mater. **1998**, *46* (13), 4543.

843. Noh, H.; Flanagan, T.B.; Sakamoto, Y. Hydrogen-induced segregation in Pd–Pt alloys. J. Alloys Compd. **1995**, *231*, 10.

844. Noh, H.; Clewley, J.D.; Flanagan, T.B.; Craft, A.P. Hydrogen-induced phase separation in Pd–Rh alloys. J. Alloys Compd. **1996**, *240*, 235.

845. Flanagan, T.B.; Noh, H. A possible role for hydrogen-induced lattice migration in alloy materials processing. J. Alloys Compd. **1995**, *231*, 1.

846. Flanagan, T.B.; Park, C.-N. Hydrogen-induced rearrangements in Pd-rich alloys. J. Alloys Compd. **1999**, *293–295*, 161.

847. Keuler, J.N.; Lorenzen, L.; Sanderson, R.D.; Prozesky, V.; Przybylowicz, W.J. Characterization of electroless plated palladium–silver alloy membranes. Thin Solid Films **1999**, *347* (1–2), 91.

848. Keuler, J.N.; Lorenzen, L.; Sanderson, R.D.; Prozesky, V.; Przybylowicz, W.J. Characterising palladium–silver and palladium–nickel alloy membranes using SEM, XRD and PIXE. Nucl. Instrum. Methods Phys. Res., Sect. B **1999**, *158*, 678.

849. Yamauchi, S.; Taura, T.; Isogai, Y.; Seino, H. Hydrogen Permeable Membrane and Hydrogen Permeating Assembly. US Patent 3,469,372, Sep. 30, 1969.

850. Ogawa, M.; Kobayashi, T.; Sueda, M.; Matsumoto, T.; Imai, T.; Shirogane, S.; Shiota, H.; Uchida, T.; Ota, S. Hydrogen Separation Member. US Patent 5,782,960, Jul. 21, 1998.

851. Haley, F.C. Gas Analysis Systems and Palladium Tube Separator Therefor. US Patent 3,791,106, Feb. 12, 1974.

852. Bredesen, R.; Klette, H. Method of Manufacturing Thin Metal Membranes. US Patent 6,086,729, Jul. 11, 2000.

853. Soria, R. Overview on industrial membranes. Catal. Today **1995**, *25*, 285.

854. Krishnan, G.N.; Damle, A.S.; Sanjurjo, A.; Wood, B.J.; Lau, K.-H. In *Thermal/Chemical Degradation of Inorganic Membrane Materials*, Proceedings of the Advanced Coal-fired Power Systems ’95 Review Meeting, Morgantown, West Virginia, US, 1995; McDaniel, H., Mollot, D.J., Venkataraman, V.K., Eds.; US DOE667.

855. Ha, H.Y.; Nam, S.W.; Lim, T.H.; Oh, I.-H.; Hong, S.-A. Properties of the $TiO_2$ membranes prepared by CVD of titanium tetraisopropoxide. J. Membr. Sci. **1996**, *111*, 81.

856. Chang, C.H.; Gopalan, R.; Lin, Y.S. A comparative study on thermal and hydrothermal stability of alumina, titania, and zirconia membranes. J. Membr. Sci. **1994**, *91*, 27.

857. Lin, Y.-S.; Chang, C.-H.; Gopalan, R. Improvement of thermal stability

of porous nanostructured ceramic membranes. Ind. Eng. Chem. Res. **1994**, *33*, 860.

858. Kim, J.; Lin, Y.S. Palladium-modified yttria-stablilized zirconia membranes. Ind. Eng. Chem. Res. **2000**, *39* (6), 2124.
859. Jarosch, K.; de Lasa, H.I. Novel riser simulator for methane reforming using high temperature membranes. Chem. Eng. Sci. **1999**, *54*, 1455.
860. Masuda, H.; Nishio, K.; Baba, N. Preparation of microporous metal membrane using two-step replication of interconnected structure of porous glass. J. Mater. Sci. Lett. **1994**, *13* (5), 338.
861. Itoh, N.; Shindo, Y.; Haraya, K.; Hakuta, T. A membrane reactor using microporous glass for shifting equilibrium of cyclohexane dehydrogenation. J. Chem. Eng. Jpn. **1988**, *21* (4), 399.
862. Gryaznov, V.M.; Karavanov, A.N.; Krasil'nikova, O.K.; Chernyshova, G.L.; Patrikeev, A.V. Palladium on mesoporous glass as a catalyst for hydrogenation of unsaturated compounds. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1981**, *30* (7), 1353.
863. Cannon, K.C.; Hacskaylo, J.J. Evaluation of palladium-impregnation on the performance of a Vycor glass catalytic membrane reactor. J. Membr. Sci. **1992**, *65*, 259.
864. Ha, H.Y.; Nam, S.W.; Hong, S.-A.; Lee, W.K. Chemical vapor deposition of hydrogen-permselective silica films on porous glass supports from tetraethylorthosilicate. J. Membr. Sci. **1993**, *85*, 279.
865. Randon, J.; Mardilovich, P.P.; Govyadinov, A.N.; Paterson, R. Computer simulation of inorganic membrane morphology part 3. Anodic alumina films and membranes. J. Colloid Interface Sci. **1995**, *169* (2), 335.
866. Konno, M.; Shindo, M.; Sugawara, S.; Saito, S. A composite palladium and porous aluminum oxide membrane for hydrogen gas separation. J. Membr. Sci. **1988**, *37*, 193.
867. Itoh, N.; Tomura, N.; Tsuji, T.; Hongo, M. Deposition of palladium inside straight mesopores of anodic alumina tube and its hydrogen permeability. Microporous Mesoporous Mater. **2000**, *39*, 103.
868. Itoh, N.; Kato, K.; Tsuji, T.; Hongo, M. Preparation of a tubular anodic aluminum oxide membrane. J. Membr. Sci. **1996**, *117*, 189.
869. Zhao, H.-B.; Xiong, G.-X.; Baron, G.V. Preparation and characterization of palladium-based composite membranes by electroless plating and magnetron sputtering. Catal. Today **2000**, *56* (1–3), 89.
870. de Vos, R.M.; Verweij, H. High-selectivity, high-flux silica membranes for gas separation. Science **1998**, *279*, 1710.
871. Yildirim, Y.; Gobina, E.; Hughes, R. An experimental evaluation of high-temperature composite membrane systems for propane dehydrogenation. J. Membr. Sci. **1997**, *135*, 107.
872. Gobina, E.; Hou, K.; Hughes, R. Ethane dehydrogenation in a catalytic

membrane reactor coupled with a reactive sweep gas. Chem. Eng. Sci. **1995**, *50* (14), 2311.

873. Gobina, E.; Hou, K.; Hughes, R. Equilibrium-shift in alkane dehydrogenation using a high-temperature catalytic membrane reactor. Catal. Today **1995**, *25* (3–4), 365.
874. Gobina, E.; Hughes, R. Ethane dehydrogenation using a high-temperature catalytic membrane reactor. J. Membr. Sci. **1994**, *90*, 11.
875. Deng, J.; Wu, J. Formaldehyde production by catalytic dehydrogenation of methanol in inorganic membrane reactors. Appl. Catal., A **1994**, *109* (1), 63.
876. Nam, S.-E.; Lee, S.-H.; Lee, K.H. Preparation of a palladium alloy composite membrane supported in a porous stainless steel by vacuum electrodeposition. J. Membr. Sci. **1999**, *153*, 163.
877. Garnier, O.; Shu, J.; Grandjean, B.P.A. Membrane-assisted two-step process for methane conversion into hydrogen and higher hydrocarbons. Ind. Eng. Chem. Res. **1997**, *36* (3), 553.
878. Lin, Y.-M.; Rei, M.-H. Study on the hydrogen production from methanol steam reforming in supported palladium membrane reactor. Catal. Today **2001**, *67*, 77.
879. Li, A.; Liang, W.; Hughes, R. Characterisation and permeation of palladium/stainless steel composite membranes. J. Membr. Sci. **1998**, *149* (2), 259.
880. Li, A.; Lian, W.; Hughes, R. Fabrication of dense palladium composite membranes for hydrogen separation. Catal. Today **2000**, *56* (1–3), 45.
881. Pierce, R.W. Method for Making a Fine Porosity Filter Element. US Patent 3,241,298, Mar. 22, 1966.
882. Jemaa, N.; Shu, J.; Kaliaguine, S.; Grandjean, P.A. Thin palladium film formation on shot peening modified porous stainless steel substrates. Ind. Eng. Chem. Res. **1996**, *35*, 973.
883. Castelli, S.; Bimbi, L.; De Francesco, M.; Iasonna, A.; Tosti, S.; Violante, V. In *Deposition of a Pd–Ag Film Alloy on Macroporous Ceramic Supports*, 20th Symp. Fusion Technol., Marseille, France, Sept. 7–11, 1998; 993.
884. Ye, J.; Dan, G.; Yuan, Q. The preparation of ultrathin palladium membrane. Key Eng. Mater. **1991**, *61,62*, 437.
885. Edlund, D.; Newbold, D.; Frost, C. Composite Hydrogen Separation Element and Module. US Patent 5,645,626, Jul. 8, 1997.
886. Behr, F.; Kugler, B.; Pietsch, M.; Weirich, W. Non-porous Hydrogen Diffusion Membrane and Utilization thereof. US Patent 4,781,734, Nov. 1, 1988.
887. Hill, E.F. Hydrogen Separation Using Coated Titanium Alloys. US Patent 4,468,235, Aug. 28, 1984.

888. Buxbaum, R.E.; Hsu, P.C. Measurement of diffusive and surface transport resistances for deuterium in palladium-coated zirconium membranes. J. Nucl. Mater. **1992**, *189* (1), 183.

889. Radzhabov, T.D.; Alimova, L.Y.; Zhukova, E.Y.; Melkumyan, F.S. Effect of thin-film coatings on the hydrogen permeability of metals. Russ. J. Phys. Chem. **1980**, *54* (11), 1605.

890. Stokes, C.L.; Buxbaum, R.E. Analysis of palladium coatings to remove hydrogen isotopes from zirconium fuel rods in Canada deuterium uranium-pressurized heavy water reactors: thermal and neutron diffusion effects. Nucl. Technol. **1991**, *98*, 207.

891. Gol'tsov, V.A.; Latyshev, V.V.; Alekhov, A.A. A unit for measuring the parameters of penetration of hydrogen isotopes through metal membranes. Sov. Mater. Sci. (Fiz.-Khim. Mekh. Mater.) **1977**, *13* (3), 338.

892. Meunier, G.; Manaud, J.-P.; Devalette, M. Ètude comparative de la diffusion de l'hydrogène à travers des membranes d'alliage palladium–argent, de nickel et de monel. J. Less-Common Met. **1981**, *77*, P47.

893. Meunier, G.; Manaud, J.P. Thin film permeation membranes for hydrogen purification. Int. J. Hydrogen Energy **1992**, *17* (8), 599.

894. Meunier, G.; Manaud, J.-P.; Devalette, M. Purification de l'hydrogene. Entropie **1984**, *20* (116–117), 26.

895. Telkov, V.I.; Andreev, L.A.; Malyutina, G.L. The influence of surface processes on the permeability of thin nickel membranes to hydrogen. Russ. J. Phys. Chem. **1980**, *54* (11), 1573.

896. Stickney, R.E.; Bradley, T.L.; Kenney, T.E.; Levin, R.L. Permeation of hydrogen through Ni, Fe, Pt, Nb, Cu, and stainless steel at elevated temperatures: Surface effects. Ber. Bunsen-Ges. **1972**, *76* (8), 760.

897. Brass, A.M.; Chene, J.; Boutry-Forveille, A. SIMS analysis of deuterium distribution in palladium coatings on pure iron. Corros. Sci. **1994**, *36* (4), 707.

898. Baker, R.W.; Louie, J.P; Pfromm, P.H.; Wijmans, J.G. Ultrathin Composite Metal Membranes. US Patent 4,857,080, Aug. 15, 1989.

899. Mercea, P.V.; Silipas, D.; Mecea, V. Separation of a gas mixture through a polymer membrane metallized with palladium. Gas Sep. Purif. **1990**, *4*, 137.

900. Beu, T.A.; Mercea, P.-V. Gas transport through metallized polymer membranes. Mater. Chem. Phys. **1990**, *26*, 309.

901. Mercea, P.; Muresan, L.; Mecea, V. Permeation of gases through metallized polymer membranes. J. Membr. Sci. **1985**, *24*, 297.

902. Mercea, P.; Muresan, L.; Silipas, D.; Ursu, I. Permeation of gases through poly(ethyleneterephthalate) membranes metallized with palladium. J. Membr. Sci. **1988**, *35*, 291.

903. Ermilova, M.M.; Gogua, L.D.; Gryaznov, V.M.; Zavodchenko, S.I. Gas

permeability of composite membrane catalysts. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1980**, *29* (4), 529.

904. Gryaznov, V.M.; Ermilova, M.M.; Zavodchenko, S.I.; Orekhova, N.V. Hydrogen permeability of some metallopolymer membranes. Polym. Sci. U. S. S. R. (Vysokomol. Soedin., Ser. A) **1993**, *35* (3), 365.
905. Gryaznov, V.M.; Smirnov, V.S.; Vdovin, V.M.; Ermilova, M.M.; Gogua, L.D.; Pritula, N.A.; Litvinov, I.A. Method of Preparing a Hydrogen-permeable Membrane Catalyst on a Base of Palladium or Its Alloys for the Hydrogenation of Unsaturated Organic Compounds. US Patent 4,132,668, Jan. 2, 1979.
906. Gudeleva, N.N.; Nogerbekov, B.Y.; Mustafina, R.G. Hydrogenation of sodium p-nitrophenoxide on a palladium-containing cation exchange membrane. Kinet. Catal. **1987**, *29* (6), 1299.
907. Gudeleva, N.N.; Nogerbekov, B.Y.; Mustafina, R.G.; Kobets, N.V. Study of nitro group reduction on membrane catalysts in acid medium. J. Appl. Chem. USSR (Zh. Prikl. Khim.) **1989**, *62* (8), 1698.
908. Yu, Z.; Xu, Y.; Liao, S.; Liu, R. Catalytic behaviors and gas permeation properties of palladium-containing phenophthalein poly(ether sulfone). J. Appl. Polym. Sci. **1996**, *61*, 599.
909. Gao, H.; Xu, Y.; Liao, S.; Liu, R.; Yu, D. Catalytic hydrogenation and gas permeation properties of metal-containing poly(phenylene oxide) and polysulfone. J. Appl. Polym. Sci. **1993**, *50*, 1035.
910. Fritsch, D.; Peinemann, K.-V. Catalysis with homogeneous membranes loaded with nanoscale metallic clusters and their preparation. Catal. Today **1995**, *25* (3–4), 277.
911. Bottino, A.; Capannelli, G.; Grosso, A.; Monticelli, O.; Cavalleri, O.; Rolandi, R.; Soria, R. Surface characterization of ceramic membranes by atomic force microscopy. J. Membr. Sci. **1994**, *95*, 289.
912. Franz, A.J.; Jensen, K.F.; Schmidt, M.A. In *Palladium Based Micromembranes for Hydrogen Separation and Hydrogenation/Dehydrogenation Reactions*, 12th Intl. Workshop on Micro Electro Mechanical Systems—MEMS, Orlando, Florida, Jan. 17–21, 1999; IEEE: Piscataway, New Jersey, US382.
913. Frankel, F. Envisioning science—a personal perspective. Science **1998**, *280*.
914. Gol'stov, V.A.; Artemenko, Y.A. Gaseous hydrogen pressure effects on the morphological and kinetic properties of the hydride transformations in a thermodynamically open palladium–hydrogen system. Phys. Met. Metallogr. **1994**, *78* (4), 432.
915. Jun, C.S.; Lee, K.H. Preparation of palladium membranes from the reaction of Pd($C_3H_3$)($C_5H_5$) with $H_2$: Wet-impregnated deposition. J. Membr. Sci. **1999**, *157* (1), 107.

916. Noh, H.; Flanagan, T.B.; Sakamoto, Y. Hydrogen-induced segregation in Pd–Pt alloys. Scr. Metall. **1993**, *29*, 445.
917. Batyrev, I.G.; Karavanov, A.N.; Leiro, J.A.; Heinonen, M. X-ray photoelectron and Auger spectroscopic studies of surface segregation in Pd-based alloys. Russ. J. Phys. Chem. **1994**, *68* (8), 1311.
918. Batyrev, I.G.; Leiro, J.A. Changes in the density of electron states caused by surface segregation in Pd–Ru, P–Ni, and Pd–Co alloys. Russ. J. Phys. Chem. **1994**, *68* (8), 1315.
919. Batirev, I.G.; Karavanov, A.N.; Leiro, J.A.; Heinonen, M.; Juhanoja, J. X-ray photoelectron and Auger electron spectroscopies and surface segregations in Pd–Rh and Pd–Ru membrane catalysts. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1994**, *23* (1), 50.
920. Batirev, I.G.; Karavanov, A.N.; Leiro, J.A.; Heinonen, M.; Juhanoja, J. X-ray photoelectron and Auger electron spectroscopies and surface segregations in Pd–Rh and Pd–Ru membrane catalysts. Surf. Interface Anal. **1995**, *23* (1), 50.
921. Haack, L.P.; Otto, K. X-ray photoelectron spectroscopy of Pd/γ-alumina and Pd foil after catalytic methane oxidation. Catal. Lett. **1995**, *34*, 31.
922. Asami, N.; Senjuh, T.; Kamimura, H.; Sumi, M.; Kennel, E.; Sakai, T.; Mori, K.; Watanabe, H.; Matsui, K. Material characteristics and behaviour of highly deuterium loaded palladium by electrolysis. J. Alloys Compd. **1997**, *253–254*, 185.
923. Antoniazzi, A.B.; Haasz, A.A.; Auciello, O.; Stangeby, P.C. Atomic, ionic and molecular hydrogen permeation facility with in situ Auger surface analysis. J. Nucl. Mater. **1984**, *128 & 129*, 670.
924. Ilias, S.; Su, N.; Udo-Aka, U.I.; King, F.G. Application of electroless deposited thin-film palladium composite membrane in hydrogen separation. Sep. Sci. Technol. **1997**, *32* (1–4), 487.
925. Collins, J.P.; Way, J.D. Hydrogen-selective Membrane. US Patent 5, 652,020, Jul. 29, 1997.
926. Shu, J.; Bongondo, B.E.W.; Grandjean, B.P.A.; Adnot, A.; Kaliaguine, S. Surface segregation of Pd–Ag membranes upon hydrogen permeation. Surf. Sci. **1993**, *291*, 129.
927. Shu, J.; Bongondo, B.E.W.; Grandjean, B.P.A.; Kaliaguine, S. Morphological changes of Pd–Ag membranes upon hydrogen permeation. J. Mater. Sci. Lett. **1997**, *16* (4), 294.
928. Shu, J.; Grandjean, B.P.A.; Kaliaguine, S. Asymmetric Pd–Ag/stainless steel catalytic membranes for methane steam reforming. Catal. Today **1995**, *25* (3–4), 327.
929. Shu, J.; Grandjean, B.P.A.; Kaliaguine, S. Effect of $Cu(OH)_2$ on electroless copper plating. Ind. Eng. Chem. Res. **1997**, *36* (5), 1632.

930. Shu, J.; Grandjean, B.P.A.; Kaliaguine, S. Gas permeation and isobutane dehydrogenation over very thin Pd/ceramic membranes. Can. J. Chem. Eng. **1997**, *75* (4), 712.

931. Shu, J.; Grandjean, B.P.A.; Kaliaguine, S.; Ciaveralla, P.; Giroir-Fendler, A.; Dalmon, J.-A. Ultrathin Pd/ceramic membranes: Preparation, permeation and application in isobutane dehydrogenation. Can. J. Chem. Eng. **1995** (Nov.), *73*.

932. Huang, T.-C.; Wei, M.-C.; Chen, H.-I. In *Study of Hydrogen Permeation Through Palladium/Alumina Composite Membranes*, Proc. 5th Intl. Conf. Inorganic Membr., Nagoya, Japan, June 22–26, 1998; 580.

933. Allmendinger, T. Electrochemical Process for Manufacturing Membrane Based on Palladium and Supported Metallic Element. EP Patent 358727, 1990.

934. Iniotakis, N.; von der Decken, C.-B.; Fedders, H.; Fröhling, W.; Sernetz, F. Hydrogen Permeation Membrane. US Patent 4,699,637, Oct. 13, 1987.

935. Poschmann, T. Verwendung einer Metallmembranfolie aus einer Palladiumlegierung zur Wasserstoffabtrennung. EP Patent 908536A2, 1998.

936. More effective hydrogen filters. Mech. Eng. **1996**, *118* (3), 14.

937. Winkelmann, U.; Schulten, R.; Weirich, W.; Kügler, B.; Lücke, L.; Oertel, M.; Pietsch, M.; Schmitz, J. Nichtporöse Metallmembranen zur selektiven Abtrennung von Wasserstoff aus Gasgemischen bei hohen Temperaturen. Chem.-Ing.-Tech. **1986**, *58* (10), 824.

938. Behr, F.; Schulten, R.; Weirich, W. Diffusion Membrane and Process for Separating Hydrogen from Gas Mixture. US Patent 4,496,373, Jan. 29, 1985.

939. Fujimoto, Y.; Tadayyon, S.-M.; Yoshinari, O.; Tanaka, K. Effect of hydriding on structural stability of Ni/Ti and Pd/Ti multilayers. Mater. Trans., JIM **1997**, *38* (9), 780.

940. Edlund, D.J.; Friesen, D.T.; Brooke, J.W.; LaChapelle, E.D. In *Composition and Properties of a Novel Hydrogen-permeable Composite Metal Membrane*, Proc. 1990 Intl. Congress on Membranes and Membr. Proc., 1990; 1019.

941. Ma, Y.H.; Mardilovich, P.P.; She, Y. Hydrogen Gas-extraction Module and Method of Fabrication. US Patent 6,152,987, Nov. 28, 2000.

942. Franz, A.J.; Jensen, K.F.; Schmidt, M.A.; Firebaugh, S. Integrated Palladium-based Micromembranes for Hydrogen Separation and Hydrogenation/Dehydrogenation Reactions. WO Patent 0032512, Jun. 8, 2000.

943. Quiram, D.J.; Hsing, I.-M.; Franz, A.J.; Jensen, K.F.; Schmidt, M.A. Design issues for membrane-based, gas phase microchemical systems. Chem. Eng. Sci. **2000**, *55*, 3065.

944. Arita, T.; Yamanashi, T.; Okuno, K.; Yamamoto, I. Experimental study

of separative characteristics of cryogenic-wall thermal diffusion column for H–D and H–T mixtures. Fusion Eng. Des. **1998**, *39–40*, 1021.

945. Yamamoto, I.; Kobayashi, N.; Kanagawa, A. State of the art of separative analysis of cryogenic-wall thermal diffusion column for hydrogen isotope separation. Fusion Technol. **1995**, *28*, 785.
946. Cui, T.; Fang, J.; Zheng, A.; Jones, F.; Reppond, A. Fabrication of microreactors for dehydrogenation of cyclohexane to benzene. Sens. Actuators, B **2000**, *B71*, 228.
947. Xomeritakis, G.; Lin, Y.S. Fabrication of thin metallic membranes by MOCVD and sputtering. J. Membr. Sci. **1997**, *133* (2), 217.
948. Bryden, K.J.; Ying, J.Y. Nanostructured palladium membrane synthesis by magnetron sputtering. Mater. Sci. Eng., A **1995**, *204* (1), 140.
949. Yan, S.; Maeda, H.; Kusakabe, K.; Morooka, S. Thin palladium membrane formed in support pores by metal-organic chemical vapor deposition method and application to hydrogen separation. Ind. Eng. Chem. Res. **1994**, *33*, 616.
950. Kusakabe, K.; Yokoyama, S.; Morooka, S.; Hayashi, J.-i.; Nagata, H. Development of supported thin palladium membrane and application to enhancement of propane aromatization on Ga-silicate catalyst. Chem. Eng. Sci. **1996**, *51* (11), 3027.
951. Wang, T.K.; Baker, J.W. Planar Palladium Structure. US Patent 5,734,092, Mar. 31, 1998.
952. Huang, L.; Chen, C.S.; He, Z.D.; Peng, D.K.; Meng, G.Y. Palladium membranes supported on porous ceramics prepared by chemical vapor deposition. Thin Solid Films **1997**, *302*, 98.
953. Nicolas, M.; Burger, J.P.; Dumoulin, L. Hydrogen absorption at 170 K in thin Pd–Ni films. Z. Phys. Chem. N.F. **1989**, *163*, 67.
954. Salomons, E.M.; Feenstra, R.; de Groot, D.G.; Rector, J.H.; Griessen, R. Pressure-composition isotherms of thin $PdH_c$ films. J. Less-Common Met. **1987**, *130*, 415.
955. Meng, G.Y.; Huang, L.; Pan, M.; Chen, C.S.; Peng, D.K. Preparation and characterization of Pd and Pd–Ni alloy membranes on porous substrates by MOCVD with mixed metal β-diketone precursors. Mater. Res. Bull. **1997**, *32* (4), 385.
956. Deshpande, A.J.; Toops, T.; Collins, J.P.; Ward, T.L. In *Fabrication of Metal Membranes by Aerosol–Particle and Chemical–Vapor–Deposition Routes*, N. American Membr. Soc. 7th Annual Mtg., 1995.
957. Liu, B.; Cao, Y.; Deng, J. Catalytic dehydrogenation of ethanol in Ru-modified alumina membrane reactor. Sep. Sci. Technol. **1997**, *32* (10), 1683.
958. Li, A.; Xiong, G.; Gu, J.; Zheng, L. In *Pd/Alumina Composite Membrane: A New Preparation Technique and Application in Catalytic*

*Reaction*, 4th International Conference on Inorganic Membranes, Gatlinburg, Tennessee, Jul. 14–18, 1996; Fain, D., Ed.; 480.

959. Zhao, H.B.; Xiong, G.X.; Gu, J.H.; Sheng, S.S.; Bauser, H.; Stroh, N.; Pflanz, K. Preparation and characterization of novel porous metal/ceramic catalytic membrane materials. Catal. Today **1995**, *25* (3–4), 237.
960. Szegner, J.; Yeung, K.L.; Varma, A. Effect of catalyst distribution in a membrane reactor: experiments and model. AIChE J. **1997**, *43* (8), 2059.
961. Lee, S.-Y.; Lee, S.-J.; Kwon, S.-J.; Yang, S.-M.; Park, S.B. Preparation of sol-gel driven alumina membrane modified by soaking and vapor deposition method. J. Membr. Sci. **1995**, *108*, 97.
962. Uhlhorn, R.J.R.; Zaspalis, V.T.; Keizer, K.; Burggraaf, A.J. Synthesis of ceramic membranes: Part II. Modification of alumina thin films: Reservoir method. J. Mater. Sci. **1992**, *27*, 538.
963. Li, Z.Y.; Naeda, H.; Kusakabe, K.; Morooka, S.; Anzai, H.; Akiyama, S. Preparation of palladium–silver alloy membranes for hydrogen separation by the spray pyrolysis method. J. Membr. Sci. **1993**, *78*, 247.
964. Basile, A.; Violante, V.; Santella, F.; Drioli, E. Membrane integrated system in the fusion reactor fuel cycle. Catal. Today **1995**, *25* (3–4), 321.
965. Basile, A.; Criscuoli, A.; Santella, F.; Drioli, E. Membrane reactor for water gas shift reaction. Gas Sep. Purif. **1996**, *10* (4), 243.
966. Barbieri, G.; Di Maio, F.P. Simulation of the methane steam re-forming process in a catalytic Pd-membrane reactor. Ind. Eng. Chem. Res. **1997**, *36*, 2121.
967. Vitulli, G.; Pitzalis, E.; Salvadori, P.; Capannelli, G.; Monticelli, O.; Servida, A.; Julbe, A. Porous Pt/$SiO_2$ catalytic membranes prepared using mesitylene solvated Pt atoms as a source of Pt particles. Catal. Today **1995**, *25* (3–4), 249.
968. Fernandes, N.E.; Fisher, S.M.; Poshusta, J.C.; Vlachos, D.G.; Tsapatsis, M.; Watkins, J.J. Reactive deposition of metal thin films within porous supports from supercritical fluids. Chem. Mater. **2001**, *13* (6), 2023.
969. Caga, I.T.; Winterbottom, J.M.; Harris, I.R. Pd-based hydrogen diffusion membranes as catalysts in carbon monoxide hydrogenation. Catal. Lett. **1989**, *3*, 309.
970. Caga, I.T.; Winterbottom, J.M.; Harris, I.R. Pd-based diffusion membranes as ethylene hydrogenation catalysts. Inorg. Chim. Acta **1987**, *140*, 53.
971. Sakai, O.; Kawae, T.; Takahashi, T. Apparatus for Recovering, Refining, and Storing Hydrogen Gas. EP Patent 0854111, Jul. 22, 1998.
972. Sakai, O.; Nakamura, S.; Kawae, T.; Yoshida, H. Production of Gas Separating Body. Japan Patent JP 8266876, 1996.
973. Kawae, T.; Kosaka, S.; Nakamura, S. Gas Separator. EP Patent 822161, 1998.

974. Kawae, T.; Takahashi, T.; Sakai, O. Apparatus for Keeping and Improving Purity of Hydrogen. Japan Patent JP 10203802, 1998.
975. Lu, S.-Y.; Lin, Y.-Z. Pd–Ag alloy films prepared by metallorganic chemical vapor deposition process. Thin Solid Films **2000**, *376*, 67.
976. Bryden, K.J.; Ying, J.Y. Synthesis and structural characteristics of mechnically alloyed nanostructured palladium–yttrium. Mater. Sci. Forum. **1996**, *225–227* (2), 895.
977. Trudeau, M.L.; Bryden, K.J.; Braunovic, M.; Ying, J.Y. Fretting studies of nanocrystalline Pd, Pd–Ag and Pd–Y films. Nanostruct. Mater. **1997**, *9*, 759.
978. Weil, R. The origins of stress in electrodeposits: Review of the literature dealing with stress in electrodeposited metals. Plating **1971**, *58* (2), 137.
979. Swanson, M.L. *Gas Separation and Hot-gas Cleanup: Topical Report, DE96004447*; University of North Dakota: Grand Forks, North Dakota, US, 1996.
980. Mleczko, L.; Ostrowski, T.; Wurzel, T. A fluidised-bed membrane reactor for the catalytic partial oxidation of methane to synthesis gas. Chem. Eng. Sci. **1996**, *51* (11), 3187.
981. Kumpmann, A.; Günther, B.; Kunze, H.-D. Thermal stability of ultrafine-grained metals and alloys. Mater. Sci. Eng., A **1993**, *168*, 165.
982. Foo, K.Y. Hydrogen Separation in Palladium Ceramic Membranes and Palladium–Gold Ceramic Membranes. M.S. Thesis; Colorado School of Mines: Golden, Colorado, US, 1995.
983. Höllein, V.; Thornton, M.; Quicker, P.; Dittmeyer, R. Preparation and characterization of palladium composite membranes for hydrogen removal in hydrocarbon dehydrogenation reactors. Catal. Today **2001**, *67*, 33.
984. Paglieri, S.N. Palladium and Palladium–Copper Composite Membranes for Hydrogen Separation. Ph.D. Thesis; Colorado School of Mines: Golden, Colorado, US, 1999.
985. Edlund, D.J. Composite Hydrogen Separation Element and Module. US Patent 5,498,278, Mar. 12, 1996.
986. Li, A.; Liang, W.; Hughes, R. Repair of a Pd/$\alpha$–$Al_2O_3$ composite membrane containing defects. Sep. Purif. Technol. **1999**, *15* (2), 113.
987. Morooka, S.; Kusakabe, K. Microporous inorganic membranes for gas separation. MRS Bull. **1999**, *24* (3), 25.
988. Morooka, S.; Kusakabe, K. Inorganic membranes for gas separation at elevated temperatures. Ind. Ceram. **2000**, *20* (1), 15.
989. Loy, D.A. *Development of New Hybrid Organic–Inorganic Materials for Hydrogen Separation Membranes at Sandia National Laboratories, SAND2000-1888C (DE00761835)*; Sandia National Laboratory: Albuquerque, New Mexico, US, 2000.

990. Tsapatsis, M.; Kim, S.; Nam, S.W.; Gavalas, G. Synthesis of hydrogen permselective $SiO_2$, $TiO_2$, $Al_2O_3$, and $B_2O_3$ membranes from the chloride precursors. Ind. Eng. Chem. Res. **1991**, *30*, 2152.

991. Prabhu, A.K.; Oyama, S.T. Highly hydrogen selective ceramic membranes: Application to the transformation of greenhouse gases. J. Membr. Sci. **2000**, *176*, 233.

992. Uhlhorn, R.J.R.; Keizer, K.; Burggraaf, A.J. Gas transport and separation with ceramic membranes. Part II. Synthesis and separation properties of microporous membranes. J. Membr. Sci. **1992**, *66*, 271.

993. Lee, L.-L.; Tsai, D.-S. A hydrogen-permselective silicon oxycarbide membrane derived from polydimethlysilane. J. Am. Ceram. Soc. **1999**, *82* (10), 2796.

994. Gavalas, G.R.; Megiris, C.E.; Nam, S.W. Deposition of $H_2$-permselective $SiO_2$ films. Chem. Eng. Sci. **1989**, *44* (9), 1829.

995. Raman, N.K.; Ward, T.L. Catalyst dispersion on supported ultramicroporous inorganic membranes using derivatized silylation agents. Appl. Catal., A **1993**, *96* (1), 65.

996. Yan, S.; Maeda, H.; Kusakabe, K.; Morooka, S.; Akiyama, Y. Hydrogen-permselective $SiO_2$ membrane formed in pores of alumina support tube by chemical vapor deposition with tetraethyl orthosilicate. Ind. Eng. Chem. Res. **1994**, *33*, 2096.

997. Morooka, S.; Kusakabe, K. In *Separation of Hydrogen from $H_2$–$H_2O$–HBr System at High Temperature with Supported $SiO_2$ Membrane*, 11th World Hydrogen Energy Conference, Stuttgart, Germany, 1996.

998. Ioannides, T.; Verykios, X. Application of a dense silica membrane reactor in the reactions of dry reforming and partial oxidation of methane. Catal. Lett. **1996**, *36*, 165.

999. Rao, M.B.; Sircar, S.; Golden, T.C. Gas Separation by Adsorbent Membranes. US Patent 5,104,425, 1992.

1000. Thaeron, C.; Parrillo, D.J.; Sircar, S.; Clarke, P.F.; Paranjape, M.; Pruden, B.B. Separation of hydrogen sulfide–methane mixtures by selective surface flow membrane. Sep. Purif. Technol. **1999**, *15*, 121.

1001. Shakhbazov, S.D.; Akhmedov, Z.G.; Rzaev, P.F.; Velieva, B.A. Possibilities of separating water thermolysis products in solar furnaces. Appl. Sol. Energy (Geliotekhnika) **1977**, *13* (6), 57.

1002. Sokol'skii, D.V.; Gudeleva, N.N.; Nogerbekov, B.Y. Effect of sodium p-nitrophenolate hydrogenation on hydrogen permeation of nickel membranes. Sov. Electrochem. (Elektrokhimiya) **1988**, *24* (7), 916.

1003. Sakamoto, Y.; Baba, K.; Kurahashi, W.; Takao, K.; Takayama, S. Diffusion of hydrogen in some amorphous alloys. J. Non-Cryst. Solids **1984**, *61 & 62*, 691.

1004. Lee, Y.S.; Stevenson, D.A. Hydrogen permeation in amorphous Cu–Ti and Pd–Si alloys. J. Non-Cryst. Solids **1985**, *72*, 249.

1005. Itoh, N.; Xu, W.-C.; Hara, S.; Kimura, H.M.; Masumoto, T. Permeability of hydrogen in amorphous $Pd_{(1-x)}Si_x$ alloys at elevated temperatures. J. Membr. Sci. **1998**, *139* (1), 29.

1006. Itoh, N.; Xu, W.-C.; Hara, S.; Kimura, H.M.; Masumoto, T. Solubility of hydrogen in amorphous $Pd_{1-x}Si_x$ alloys as hydrogen permeable membranes. J. Membr. Sci. **1997**, *126*, 41.

1007. Itoh, N.; Machida, T.; Xu, W.-C.; Kimura, H.; Masumoto, T. Amorphous Pd–Si alloys for hydrogen-permeable and catalytically active membranes. Catal. Today **1995**, *25* (3–4), 241.

1008. Hara, S.; Sakaki, K.; Itoh, N.; Kimura, H.-M.; Asami, K.; Inoue, A. An amorphous alloy membrane without noble metals for gaseous hydrogen separation. J. Membr. Sci. **2000**, *164*, 289.

1009. Enick, R.M.; Morreale, B.D.; Hill, J.; Rothenberger, K.S.; Cugini, A.V.; Siriwardane, R.V.; Poston, J.A.; Balachandran, U.; Lee, T.H.; Dorris, S.E.; Graham, W.J.; Howard, B.H. Evaluation and Modeling of a High-temperature, High-pressure, Hydrogen Separation Membrane for Enhanced Hydrogen Production from the Water–Gas Shift Reaction. In *Advances in Hydrogen Energy*; Grégoire Padró, C.E., Lau, F., Eds.; Kluwer Academic/Plenum Publishers: New York, 2000; 93.

1010. Norby, T.; Larring, Y. Mixed hydrogen ion-electronic conductors for hydrogen permeable membranes. Solid State Ionics **2000**, *136–137*, 139.

1011. Condon, J.B.; Schober, T. Proton conductors and metal hydrides. Solid State Ionics **1995**, *77*, 299.

1012. Mukundan, R.; Brosha, E.L.; Birdsell, S.A.; Costello, A.L.; Garzon, F.H.; Willms, R.S. Tritium conductivity and isotope effect in proton-conducting perovskites. J. Electrochem. Soc. **1999**, *146* (6), 2184.

1013. Marnellos, G.; Kyriakou, A.; Florou, F.; Angelidis, T.; Stoukides, M. Polarization studies in the $Pd|SrCe_{0.95}Yb_{0.05}O_{2.975}|Pd$ proton conducting solid electrolyte cell. Solid State Ionics **1999**, *125*, 279.

1014. Vahldieck, N.P.; Wang, D.I.J. Method for Separating and Purifying Hydrogen by Permeation. US Patent 3,148,031, Sep. 8, 1964.

1015. Dittrich, H.; Frey, H. Apparatus for Separating Gaseous Hydrogen Isotopes. US Patent 4,528,003, Jul. 9, 1985.

1016. Teter, D.F.; Thoma, D.J. The prediction of the hydriding thermodynamics of Pd–Rh–Co ternary alloys. Metall. Mater. Trans. B **2000**, *30*, 667.

1017. Sakaguchi, H.; Yagi, Y.; Shiokawa, J.; Adachi, G. Hydrogen isotope separation using rare earth alloy films deposited on polymer membranes. J. Less-Common Met. **1989**, *149*, 185.

1018. Sakaguchi, H.; Nagai, H.; Adachi, G.; Shiokawa, J. Hydrogen separation using $LaNi_5$ films. J. Less-Common Met. **1986**, *126*, 83.

1019. Adachi, G.-Y.; Nagai, H.; Shiokawa, J. $LaNi_5$ film for hydrogen separation. J. Less-Common Met. **1984**, *97*, L9.

1020. Parrillo, D.J.; Thaeron, C.; Sircar, S. Separation of bulk hydrogen sulfide–hydrogen mixtures by selective surface flow membrane. AIChE J. **1997**, *43* (9), 2239.

1021. Sedigh, M.G.; Onstot, W.J.; Xu, L.; Peng, W.L.; Tsotsis, T.T.; Sahimi, M. Experiments and simulation of transport and separation of gas mixtures in carbon molecular sieve membranes. J. Phys. Chem. **1998**, *102* (44), 8580.

1022. Suda, H.; Haraya, K. Alkene/alkane permselectivities of a carbon molecular sieve membrane. Chem. Commun. **1997**, 93.

1023. Kusakabe, K.; Yamamoto, M.; Morooka, S. Gas permeation and micropore structure of carbon molecular sieving membranes modified by oxidation. J. Membr. Sci. **1998**, *149*, 59.

1024. Sircar, S.; Rao, M.B.; Thaeron, C.M.A. Selective surface flow membrane for gas separation. Sep. Sci. Technol. **1999**, *34* (10), 2081.

1025. Snoek, J.L.; Haes, E.J. Laboratory apparatus for the production of a steady flow of very pure hydrogen. Appl. Sci. Res. **1951**, *A2*, 326.

1026. Liu, B.; Dai, W.; Wu, G.; Deng, J.-F. Amorphous alloy/ceramic composite membrane: Preparation, characterization and reaction studies. Catal. Lett. **1997**, *49*, 181.

1027. Xue, D.; Chen, H.; Wu, G.-H.; Deng, J.-F. Amorphous Ni–B alloy membrane: Preparation and application in ethanol dehydrogenation. Appl. Catal. **2001**, *214*, 87.

1028. Sakaguchi, H.; Shirai, H.; Nishioka, K.; Suenobu, T.; Tanaka, H.; Adachi, G. Hydrogen permeability for oxide-metal multilayered films. J. Alloys Compd. **1992**, *185*, 295.

1029. Adris, A.M.; Elnashaie, S.S.E.H.; Hughes, R. A fluidized bed membrane reactor for the steam reforming of methane. Can. J. Chem. Eng. **1991**, *69*, 1061.

1030. Cohn, J.G.E.; Pfefferle, W.C. Steam Reforming with Preliminary Hydrodesulfurization. US Patent 3,595,805, Jul. 27, 1971.

1031. Kikuchi, E.; Nemoto, Y.; Kajiwara, M.; Uemiya, S.; Kojima, T. Steam reforming of methane in membrane reactors: Comparison of electroless-plating and CVD membranes and catalyst packing modes. Catal. Today **2000**, *56*, 75.

1032. Barbieri, G.; Marigliano, G.; Perri, G.; Drioli, E. Conversion-temperature diagram for a palladium membrane reactor. Analysis of an endothermic reaction: Methane steam reforming. Ind. Eng. Chem. Res. **2001**, *40* (9), 2017.

1033. Dicks, A.L. Hydrogen generation from natural gas for the fuel cell systems of tomorrow. J. Power Sources **1996**, *61*, 113.

1034. Freni, S.; Calogero, G.; Cavallaro, S. Hydrogen production from methane through catalytic partial oxidation reactions. J. Power Sources **2000**, *87*, 28.

1035. Xue, E.; O'Keeffe, M.; Ross, J.R.H. Water–gas shift conversion using a feed with a low steam to carbon monoxide ratio and containing sulphur. Catal. Today **1996**, *30*, 107.

1036. Vasileiadis, S.; Ziaka, Z. Alternative generation of $H_2$, CO and $H_2$, $CO_2$ mixtures from steam-carbon dioxide reforming of methane and the water gas shift with permeable membrane reactors. Chem. Eng. Commun. **1999**, *176*, 247.

1037. Lægsgaard Jørgensen, S.; Højlund Nielsen, P.E.; Lehrmann, P. Steam reforming of methane in a membrane reactor. Catal. Today **1995**, *25*, 303.

1038. Galuszka, J.Z.; Fouda, S.; Pandey, R.N.; Ahmed, S. Process for Producing Syngas and Hydrogen from Natural Gas Using a Membrane Reactor. US Patent 5,637,259, Jun. 10, 1997.

1039. Kim, J.-H.; Choi, B.-S.; Yi, J. Modified simulation of methane steam reforming in Pd-membrane packed-bed type reactor. J. Chem. Eng. Jpn. **1999**, *32* (6), 760.

1040. Ettouney, H.M.; Masiar, B.; Bouhamra, W.S.; Hughes, R. High temperature CO shift conversion (HTSC) using catalytic membrane reactors. Chem. Eng. Res. Des.: Trans. Inst. Chem. Eng. A **1996**, *74* (6), 649.

1041. Vandyshev, A.B.; Murav'ev, L.L.; Makarov, V.M.; Usova, T.B. Effect of reactions in the C–H–O system on the membrane extraction of especial-purity hydrogen. Chem. Pet. Eng. (Khim. Neft. Mashinostr.) **2000**, *36* (1–2), 8.

1042. Criscuoli, A.; Basile, A.; Drioli, E. An analysis of the performance of membrane reactors for the water–gas shift reaction using gas feed mixtures. Catal. Today **2000**, *56* (1–3), 53.

1043. Murav'ev, L.L.; Vandyshev, A.B.; Makarov, V.M. Modeling of membrane extraction of hydrogen from the products of steam conversion of hydrocarbons. Theor. Found. Chem. Eng. (Teor. Osn. Khim. Tekhnol.) **1999**, *33* (3), 258.

1044. Gryaznov, V.M.; Manga, I.I.; Kondrasheva, V.S.; Petrii, O.A.; Tsirlina, G.A. New possibilities of optimizing reduction of organic nitro compounds at a palladium membrane electrode modified with adatoms. Dokl. Phys. Chem. **1996**, *351* (4–6), 326.

1045. Nogerbekov, B.Y.; Gudeleva, N.N.; Kobets, N.V.; Mustafina, R.G.; Fogel', L.A. Hydrogenation of sodium p-nitrophenolate on palladium and nickel membranes. J. Appl. Chem. USSR (Zh. Prikl. Khim.) **1986**, *59* (1), 118.

1046. Nogerbekov, B.Y.; Gudeleva, N.N. Reduction of the nitro group on palladium-containing membrane catalysts in alkaline solution. Russ. J. Phys. Chem. **1996**, *70* (3), 458.

1047. Iwakura, C.; Abe, T.; Inoue, H. A new successive system for hydrogenation of styrene using a two-compartment cell separated by a Pd sheet electrode. J. Electrochem. Soc. **1996**, *143* (April), L71.

1048. Itoh, N.; Sathe, A.M. Hydrogen transport from gas to liquid phase through a palladium membrane. J. Membr. Sci. **1997**, *137*, 251.

1049. Mondal, A.M.; Ilias, S. Dehydrogenation of cyclohexane in a palladium–ceramic membrane reactor by equilibrium shift. Sep. Sci. Technol. **2001**, *36* (5 and 6), 1101.

1050. Smirnov, V.S.; Ermilova, M.M.; Kokerova, N.V.; Gryaznov, V.M. Selective hydrogenation of cyclopentadiene on membrane catalysts. Dokl. Akad. Nauk SSSR **1975**, *220* (3), 64.

1051. Moustafa, T.M.; Ashour, I.; Elnashaie, S.S. An integrated dehydrogenation hydrogenation membrane reactor for the simultaneous production of styrene and cyclohexane. Stud. Surf. Sci. Catal. **1999**, *122*, 229–236.

1052. Yeheskel, J.; Léger, D.; Courvoisier, P. Thermal Decomposition of Hydroiodic Acid and Hydrogen Separation. In *Proc. 2nd World Hydrogen Energy Conf., Zurich, Switzerland*; Veziroglu, T.N., Seifritz, W., Eds.; Pergamon Press: Elmsford, New York, 1978; 569.

1053. Reo, C.M.; Bernstein, L.A.; Lund, C.R.F. Cocurrent membrane reactors vs. PFRs for shifting dehydrogenation equilibrium. AIChE J. **1997**, *43* (2), 495.

1054. Prokopiev, S.I.; Aristov, Y.I.; Parmon, V.N.; Giordano, N. Intensification of hydrogen production via methane reforming and the optimization of $H_2$:CO ratio in a catalytic reactor with a hydrogen-permeable membrane wall. Int. J. Hydrogen Energy **1992**, *17* (4), 275.

1055. Zhernosek, V.M.; Mikhalenko, N.N.; Iokhannes, S.; Khrapova, E.V.; Gryaznov, V.M. Kinetic model for the hydrogenation of cyclopentadiene on a hydrogen-permeable catalyst. Kinet. Catal. **1979**, *20* (4), 753.

1056. Raich, B.A.; Foley, H.C. Ethanol dehydrogenation with a palladium membrane reactor: An alternative to wacker chemistry. Ind. Eng. Chem. Res. **1998**, *37* (10), 3888.

1057. Gryaznov, V.M.; Slin'ko, M.G. Selectivity in catalysis by hydrogen-porous membranes. Faraday Discuss. Chem. Soc. **1981**, *72*, 72.

1058. Ali, J.K.; Newson, E.J.; Rippin, D.W. Exceeding equilibrium conversion with a catalytic membrane reactor for the dehydrogenation of methylcyclohexane. Chem. Eng. Sci. **1994**, *49* (13), 2129.

1059. Ali, J.; Baiker, A. Dehydrogenation of methylcyclohexane to toluene in a pilot-scale membrane reactor. Appl. Catal., A **1997**, *155* (1), 41.

1060. Ali, J.K.; Baiker, A. n-Heptane reforming in a system of reactors-interstage membrane to separate hydrogen. Appl. Catal. A **1996**, *140* (1), 99.

1061. Armor, J.N.; Farris, T.S. Membrane catalysis over palladium and its alloys. Stud. Surf. Sci. Catal. **1993**, *75*, 1363.

1062. Shindo, Y.; Itoh, N.; Haraya, K. High performance reactor using a membrane. AIChE Symp. Ser. **1989**, *272* (85), 80.

1063. Sirkar, K.K.; Shanbhag, P.V.; Kovvali, A.S. Membrane in a reactor: a functional perspective. Ind. Eng. Chem. Res. **1999**, *38* (10), 3715.

1064. Gobina, E.; Hou, K.; Hughes, R. A comparative evaluation of high-temperature membrane systems for catalytic processing. Chem. Eng. Commun. **1998**, *166*, 157.

1065. Caruana, C.M. Catalytic membranes beckon. Chem. Eng. Prog. **1994**, *90* (Nov), 13.

1066. Gobina, E.; Hou, K.; Hughes, R. A reactor-separator incorporating porous and dense membrane systems. J. Chem. Technol. Biotechnol. **1997**, *70*, 74.

1067. Pena, M.A.t.o.n.; Gómez, J.P.; Fierro, J.L.G. New catalytic routes for syngas and hydrogen production. Appl. Catal. A **1996**, *144*, 7.

1068. Falconer, J.L.; Noble, R.D.; Sperry, D.P. Catalytic Membrane Reactors. In *Membrane Separations Technology. Principles and Applications*; Noble, R.D., Stern, S.A., Eds.; Elsevier Science B.V, 1995; 708.

1069. Hsieh, H.P. Inorganic membrane reactors. Catal. Rev.-Sci. Eng. **1991**, *33* (1 & 2), 1.

1070. Hsieh, H.P. *Inorganic Membranes for Separation and Reaction*; Elsevier: Amsterdam, 1996.

1071. Drioli, E.; Criscuoli, A. Microporous Inorganic and Polymeric Membranes as Catalytic Reactors and Membrane Contactors. In *Recent Advances in Gas Separation by Microporous Ceramic Membranes*; Kanellopous, N.K., Ed.; Membrane Science and Technology Series, Elsevier: New York, 2000; Vol. 6, 497.

1072. Gryaznov, V.M. Surface catalytic properties and hydrogen diffusion in palladium alloy membranes. Z. Phys. Chem. N.F. **1986**, *147*, 123.

1073. Gryaznov, V.M.; Ermilova, M.M.; Orekhova, N.V. Membrane-catalyst systems for selectivity improvement in dehydrogenation and hydrogenation reactions. Catal. Today **2001**, *67*, 185.

1074. Aguilar, G.; Gryaznov, V.M.; Pavlova, L.F.; Yagadovski, V.D. Conversion of cyclohexene on a gold-plated palladium−nickel membrane catalyst. React. Kinet. Catal. Lett. (Soobshch. Kinet. Katal.) **1977**, *7* (2), 181.

1075. Basov, N.L.; Gryaznov, V.M.; Ermilova, M.M. Hydrogenation of phenol to cyclohexanone on membrane catalysts. Russ. J. Phys. Chem. **1993**, *67* (12), 2175.

1076. Boreskov, G.K.; Gryaznov, V.M. New tendencies in the development of the science of catalysis. Kinet. Catal. **1973**, *14* (3), 711.

1077. Denisov, G.N.; Kolyagin, V.A.; Yagodovskii, V.D.; Gryaznov, V.M. The adsorption of cyclopentane, cyclopentene, and cyclopentadiene vapors on nickel and palladium films. Kinet. Catal. **1977**, *18* (3), 588.

1078. Dobrokhotov, V.G.; Gryaznov, V.M.; Pavlova, L.F. Effect of the hydrogen concentration on the adsorption and catalytic properties of a Pd–Ru alloy. J. Less-Common Met. **1983**, *89*, 585.

1079. Dobrokhotov, V.G.; Shalvashvili, E.A.; Pavlova, L.F.; Gryaznov, V.M. Adsorption of $C_6$ aliphatic hydrocarbons on Pd–Ru alloy. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1983**, *32* (7), 1342.

1080. Dobrokhotov, V.G.; Pavlova, L.F.; Gryaznov, V.M. Adsorption and hydrogenation of benzene on Pd–Ru alloy in a pulsed chromatographic regime. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1983**, *32* (5), 893.

1081. Dobrokhotov, V.G.; Reies Romero, A.; Pavlova, L.F.; Gryaznov, V.M. Conductometric study of the reaction of hydrogen, hexane, and cyclohexane with granular films of a palladium–ruthenium alloy. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1984**, *33* (12), 2439.

1082. Edussuriya, M.; Mikhalenko, N.N.; Gul'yanova, S.G.; Gryaznov, V.M.; Gomes, P. Adsorption of carbon monoxide on x-ray amorphous iron and its alloys with ruthenium. Russ. J. Phys. Chem. **1994**, *68* (11), 1905.

1083. Enikolopov, N.S.; Gryaznov, V.M.; Solov'eva, A.B.; Rish, I.G.; Zavodchenko, S.I.; Ermilova, M.M. The reduction of the central manganese ion in MnCl tetraphenylporphyrinate upon hydrogen diffusion through a palladium membrane. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1985**, *3*, 629.

1084. Ermilova, M.M.; Basov, N.L.; Smirnov, V.S.; Rumyantsev, A.N.; Gryaznov, V.M. Monomerization of dicyclopentadiene and hydrogenation of cyclopentadiene in a stream of methane over palladium–ruthenium alloy. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1979**, *28* (8), 1633.

1085. Ermilova, M.M.; Morozova, L.S.; Orekhova, N.V.; Gryaznov, V.M. The effect of catalytic hydrogenation on hydrogen transfer through a palladium–ruthenium alloy membrane. Russ. J. Phys. Chem. **1994**, *68* (7), 1094.

1086. Giller, S.A.; Gryaznov, V.M.; Pavlova, L.F.; Bulenkova, L.F.; Oshis, Y.F.; Shimanskaya, M.V. Transformations of heterocyclic compounds on membrane catalysts I. Hydrogenation of furan compounds on a Pd–Ni alloy. Chem. Heterocycl. Compd. (Khimiya Geterotsikl. Soedin.) **1975,** *10* (5), 523.

1087. Gryaznov, V.M.; Shimulis, V.I.; Yagodovskii, V.D. Relation of the catalytic properties of metals to the degree of approach of the state of their surface to equilibrium. Dokl. Akad. Nauk SSSR **1961**, *136* (5), 181.

1088. Gryaznov, V.M.; Yagodovskii, V.D.; Shimulis, V.I. The effect of thermal treatment on the catalytic properties of platinum films. Kinet. Catal. **1961**, *2* (2), 207.

1089. Gryaznov, V.M.; Polyakova, V.P.; Savitskii, E.M.; Frades, L.; Khrapova, E.V.; Khuares, E.; Shkola, G.V. Influence of the nature and amount of the second component of binary-palladium alloys on their catalytic activity with respect to the dehydrogenation of cyclohexane. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1970**, *11*, 2520.

1090. Gryaznov, V.M.; Pavlova, L.F.; Juarez, E.; Rivera, P. Differences between the catalytic transformations of cyclohexane on palladium, platinum, and rhodium. Dokl. Akad. Nauk SSSR **1970**, *194* (2), 692.

1091. Gryaznov, V.M.; Pavlova, L.F.; Rivera, P.; Rosen, A.; Khuares, E. Kinetics of cyclohexane dehydrogenation on palladium foil. Kinet. Catal. **1971**, *12* (5), 1063.

1092. Gryaznov, V.M.; Pavlova, L.F.; Khlebnikov, V.B. In *Study of Concentrations of Surface Reagents with the Help of Membrane Catalyst*, Symp. Mech. of Hydrocarbon React., Siofok, June 5–7, 1975; Am. Elsevier Sci. Publ. Co, 107.

1093. Gryaznov, V.M. Method for Carrying Out Simultaneously the Catalytic Reactions Involving Hydrogen Evolution and Consumption. US Patent 3,950,447, 1976.

1094. Gryaznov, V.M.; Smirnov, V.S. Selective hydrogenation on membrane catalysts. Kinet. Catal. **1977**, *18* (3), 485.

1095. Gryaznov, V.M.; Polyakova, V.P.; Savitsky, E.M.; Khrapova, E.V. Catalyst for Dehydrogenation or Dehydrocyclization of Hydrocarbons. US Patent 4,026,958, May 31, 1977.

1096. Gryaznov, V.M.; Zelyaeva, E.A. The formation of ammonia from nitrogen-15 and deuterium diffusing through an iron membrane catalyst. Russ. J. Phys. Chem. **1977**, *51* (1), 139.

1097. Gryaznov, V.M.; Smirnov, V.S.; Yermilova, M.M.; Orekhova, N.V.; Pavlova, L.F.; Khrapova, Y.V.; Basov, N.L.; Gogua, L.D.; Mikhalenko, N.N.; Tarasova, V.Y. Membrane catalysts in selective hydrogenation of certain products of pyrolysis of peteroleum hydrocarbons. Pet. Chem. U.S.S.R. (Neftekhimiya) **1979**, *19* (5), 165.

1098. Gryaznov, V.M.; Ermilova, M.M.; Gogua, L.D.; Orekhova, N.V.; Morozova, L.S. Selective hydrogenation of diene $C_5$ hydrocarbons on Pd–Ru membrane catalysts. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1980**, *29* (12), 1871.
1099. Gryaznov, V.M.; Ermilova, M.M.; Gogua, L.D.; Orekhova, N.V.; Morozova, L.S. Hydrogenation of cyclopentadiene in the presence of isoprene and 1,3-pentadiene on a Pd–Ru membrane catalyst. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1981**, *30* (4), 672.
1100. Gryaznov, V.M.; Ermilova, M.M.; Morozova, L.S.; Orekhova, N.V.; Polyakova, V.P.; Roshan, N.R.; Savitsky, E.M.; Parfenova, N.I. Palladium alloys as hydrogen permeable catalysts in hydrogenation and dehydrogenation reactions. J. Less-Common Met. **1983**, *89*, 529.
1101. Gryaznov, V.M.; Karavanov, A.N.; Belosljudova, T.M.; Ermolaev, A.V.; Maganjuk, A.P.; Sarycheva, I.K. Process for Producing $C_4$–$C_{10}$ Ethylene Alcohols. US Patent 4,388,479, Jun. 14, 1983.
1102. Gryaznov, V.M.; Smirnov, V.S.; Vdovin, V.M.; Ermilova, M.M.; Gogua, L.D.; Pritula, N.A.; Fedorova, G.K. Membrane Catalyst for Hydrogenation of Organic Compounds and Method for Preparing Same. US Patent 4,394,294, Jul. 19, 1983.
1103. Gryaznov, V.M.; Maganyuk, A.P.; Karavanov, A.N.; Naumov, V.A. Effect of phase composition of palladium–ruthenium membrane catalyst on selectivity of dehydrolinalool hydrogenation. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1984**, *33* (4), 853.
1104. Gryaznov, V.M. A century of studying the mechanism of catalytic reactions of hydrogen redistribution. Russ. J. Phys. Chem. **1999**, *73* (10), 1548.
1105. Gur'yanova, O.S.; Serov, Y.M.; Lapidus, A.L.; Dmitriev, R.V.; Gul'yanova, S.G.; Gryaznov, V.M.; Minachev, K.M. Absorption and disproportionation of CO on palladium alloys. Bull. Acad. Sci. USSR, Div. Chem. Sci. (Izv. Akad. Nauk SSSR, Ser. Khim.) **1987**, *36* (11), 2252.
1106. Gur'yanova, O.S.; Serov, Y.M.; Gul'yanova, S.G.; Gryaznov, V.M. Conversion of carbon monoxide on membrane catalysts of palladium alloys. I. Reaction between CO and $H_2$ on binary palladium alloys with ruthenium and nickel. Kinet. Catal. **1988**, *29* (4 (1)), 728.
1107. Gur'yanova, O.S.; Serov, Y.M.; Gur'yanova, S.G.; Gryaznov, V.M. Transformation of carbon monoxide on palladium alloy membrane catalysts. II. Reaction of CO and $H_2$ on a palladium–nickel alloy coated with dispersed nickel or copper layers. Kinet. Catal. **1989**, *30* (2), 406.
1108. Karavanov, A.N.; Gryaznov, V.M. Hydrogenation of acetylenic and ethylenic alcohols in the liquid phase on membrane catalysts consisting

of binary alloys of palladium with nickel and ruthenium. Kinet. Catal. **1984**, *25* (1), 56.

1109. Karavanov, A.N.; Gryaznov, V.M. Effect of the hydrogen content in a membrane catalyst on the selectivity of the hydrogenation of dehydrolinalool. Kinet. Catal. **1984**, *25* (1), 60.

1110. Karavanov, A.N.; Tsarevskii, N.A.; Gryaznov, V.M. Kinetics of the hydrogenation of cis- and trans-2-butene-1,4-diol on a palladium–ruthenium alloy membrane catalyst. Kinet. Catal. **1985**, *26* (1), 76.

1111. Karavanov, A.N.; Mikhalenko, N.N.; Gryaznov, V.M. Effect of transformations of hydride phases of a palladium–ruthenium alloy on the selectivity in dehydrolinalool hydrogenation. Dokl. Akad. Nauk SSSR (Dokl. Akad. Nauk SSSR) **1986**, *286* (4), 908.

1112. Karavanov, A.N.; Gryaznov, V.M. Hydrogenation of acetylene–ethylene alcohols over a palladium–ruthenium alloy membrane catalyst. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1988**, *37* (11 (1)), 2223.

1113. Karavanov, A.N.; Gryaznov, V.M. Effect of the structure of substituted propargyl and allyl alcohols on the rate of their liquid phase hydrogenation on a Pd–Ru alloy membrane catalyst. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1989**, *38* (8 (1)), 1593.

1114. Karavanov, A.N.; Gryaznov, V.M.; Roshan, N.R.; Batyrev, I.G. Palladium and its alloys as membrane catalysts for liquid-phase hydrogenation of dehydrolinalool. Kinet. Catal. **1991**, *32* (5), 1045.

1115. Karavanov, A.N.; Gryaznov, V.M.; Lebedeva, V.I.; Litvinov, I.A.; Vasil'kov, A.Y.; Olenin, A.Y. Porous membrane catalysts with Pd–M–clusters for liquid phase hydrogenation of dehydrolinalool. Catal. Today **1995**, *25* (3–4), 447.

1116. Karavanov, A.N.; Gryaznov, V.M.; Gatyrev, I.G.; Olenina, E.G. Effect of structure of unsaturated aliphatic alcohols on the hydrogenation rate over Pd–Ru membrane catalyst. Russ. J. Phys. Chem. **1995**, *69* (5), 739.

1117. Kolosov, E.N.; Starkovskii, N.I.; Gul'yanova, S.G.; Gryaznov, V.M. Oxygen permeability of thin silver membranes. I. Effect of the adsorption of benzene on the oxygen transfer process. Russ. J. Phys. Chem. **1988**, *62* (5), 661.

1118. Krasil'nikova, O.K.; Gryaznov, V.M. Study of the kinetics of sorption of hydrogen by palladium–ruthenium alloys by the method of adsorption deformation. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1988**, *37* (1 (1)), 855.

1119. Kurman, P.V.; Mardilovich, I.P.; Gryaznov, V.M.; Trokhimets, A.I. Modification of the method for temperature-programmed investigations of processes involving hydrogen absorption or evolution. Russ. J. Phys. Chem. **1995**, *69* (7), 1205.

1120. Lebedeva, V.I.; Gryaznov, V.M. Effect of hydrogen removal through a membrane catalyst on dehydrocyclization of n-hexane. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1981**, *30* (3 (2)), 452.

1121. Lebedeva, V.I.; Gryaznov, V.M. Hydrogenation of α-methylstyrene on membrane catalysts. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1988**, *37* (5), 1018.

1122. Maganyuk, A.P.; Gryaznov, V.M. Hydrogenation of organic liquids on a membrane catalyst without hydrogen pressure difference. Dokl. Phys. Chem. **1998**, *360* (4–6), 177.

1123. Mikhalenko, N.N.; Khrapova, Y.V.; Gryaznov, V.M. Effect of hydrogen transfer through a membrane catalyst from a Pd–Ru alloy on the rate of dehydrogenation of isopropanol and hydrogenation of cyclopentadiene. Pet. Chem. U.S.S.R. (Neftekhimiya) **1979**, *18* (3), 81.

1124. Mikhalenko, N.N.; Khrapova, E.V.; Gryaznov, V.M. The effect of ruthenium deposition on the catalytic properties of palladium–copper alloy foils. Russ. J. Phys. Chem. **1985**, *59* (10), 1533.

1125. Mikhalenko, N.N.; Khrapova, E.V.; Gryaznov, V.M. Influence of hydrogen on the dehydrogenation of isopropyl alcohol in the presence of a palladium membrane catalyst. Kinet. Catal. **1986**, *27* (1 (2)), 125.

1126. Mikhalenko, N.N.; Khrapova, E.V.; Gryaznov, V.M. Effect of the direction of hydrogen and cyclopentadiene vapour streams along the two surfaces of a membrane catalyst on the hydrogen permeability and on the extent of hydrogenation. Russ. J. Phys. Chem. **1986**, *60* (2), 307.

1127. Mishchenko, A.P.; Gryaznov, V.M.; Sarylova, M.E. Conversion of 1,3-pentadiene on membrane catalysts prepared from binary alloys of palladium. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1982**, *31* (7), 1312.

1128. Orekhova, N.V.; Smirnov, L.I.; Gryaznov, V.M.; Ermilova, M.M.; Mischenko, A.P. Kinetics of isoamylene dehydrogenation on a membrane catalyst. React. Kinet. Catal. Lett. (Soobshch. Kinet. Katal.) **1975**, *3* (4), 415.

1129. Orekhova, N.V.; Ermilova, M.M.; Gryaznov, V.M. Combination of cyclohexane dehydrogenation and pentadiene-1,3 hydrogenation in granulated and monolithic membrane catalyst systems. Dokl. Akad. Nauk SSSR **1992**, *321* (1), 789.

1130. Orekhova, N.V.; Ermilova, M.M.; Gryaznov, V.M. Intensification of butane dehydrogenation on a granular catalyst by hydrogen removal through palladium alloy membranes. Russ. J. Phys. Chem. **1997**, *71* (9), 1389.

1131. Rubio Barra, K.F.; Vargas Escudero, A.; Pavlova, L.F.; Gryaznov, V.M. Interaction between the products of the strong adsorption of acetylene on palladium and hydrogen. Russ. J. Phys. Chem. **1982**, *56* (10), 1603.

1132. Serov, Y.M.; Zhernosek, V.M.; Gul'yanova, S.G.; Gryaznov, V.M. Kinetics of carbon dioxide hydrogenation over a hydrogen-permeable palladium–ruthenium membrane catalyst coated with nickel. II. Kinet. Catal. **1983**, *24* (2), 303.

1133. Serov, Y.M.; Zhernosek, V.M.; Gryaznov, V.M. A kinetic model for the hydrogenation of carbon dioxide on hydrogen-permeable membrane catalysts. Kinet. Catal. **1983**, *24* (1), 207.

1134. Serov, Y.M.; Gur'yanova, O.S.; Gul'yanova, S.G.; Gryaznov, V.M. Reactions of CO on a palladium–nickel alloy saturated with hydrogen. Russ. J. Phys. Chem. **1986**, *60* (1), 117.

1135. Smirnov, V.S.; Gryaznov, V.M.; Mischenko, A.P.; Rodina, A.A. Process for Dehydrogenation, Dehydrocyclization and Hydrodealkylation of Hydrocarbons. US Patent 3,562,346, 1971.

1136. Smirnov, V.S.; Gryaznov, V.M.; Orekhova, N.V.; Ermilova, M.M.; Mishchenko, A.P. Study of the coupling of the dehydrogenation of isoamylenes with reactions of hydrogen consumption on a palladium–nickel membrane catalyst. Dokl. Akad. Nauk SSSR **1975**, *224* (2), 958.

1137. Smirnov, V.S.; Gryaznov, V.M.; Lebedeva, V.I.; Mischenko, A.P.; Polyakova, V.P.; Savitsky, E.M. Cycloparaffin Dehydrogenation to Form Aromatics Using Palladium Alloy Foil. US Patent 4,157,354, Jun. 5, 1979.

1138. Ustinova, T.S.; Shpiro, E.S.; Smirnov, V.S.; Gryaznov, V.M.; Antoshin, G.V.; Minachev, K.M. Change in composition of surface layer of palladium–rhodium alloys during catalytic reaction. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1976**, *25* (2), 441.

1139. Vedernikov, V.I.; Gryaznov, V.M.; Gul'yanova, S.G.; Deryugin, L.N.; Tishchenko, A.A.; Chernyai, A.I. Use of thin-film resonant systems in studies of the interaction of gases with metal of semiconductor film surfaces. Russ. J. Phys. Chem. **1982**, *56* (2), 297.

1140. Ito, N. Dehydrogenation by membrane reactors. Sekiyu Gakkaishi (J. Jpn. Pet. Inst.) **1990**, *33* (3), 136.

1141. Ito, N.; Shindo, Y.; Haraya, K.; Obata, K.; Hakuta, T.; Yoshitome, H. Simulation of a reaction accompanied by separation. Int. Chem. Eng. **1985**, *25* (1), 138.

1142. Ito, N. Dehydration Reaction Device. Japan Patent JP 1018437, 1989.

1143. Itoh, N. A membrane reactor using palladium. AIChE J. **1987**, *33* (9), 1576.

1144. Itoh, N. Simulation of bifunctional palladium membrane reactor. J. Chem. Eng. Jpn. **1990**, *23* (1), 81.

1145. Itoh, N. Maximum conversion of dehydrogenation in palladium membrane reactors. J. Chem. Eng. Jpn. **1991**, *24* (5), 664.

1146. Itoh, N. Development of a one-side uniform model for palladium membrane reactors. J. Chem. Eng. Jpn. **1992**, *25* (3), 336.
1147. Itoh, N. Dehydrogenation Process. US Patent 5,449,848, Sep. 12, 1995.
1148. Itoh, N. Limiting conversions of dehydrogenation in palladium membrane reactors. Catal. Today **1995**, *25* (3–4), 351.
1149. Itoh, N.; Shindo, Y.; Haraya, K. Ideal flow models for palladium membrane reactors. J. Chem. Eng. Jpn. **1990**, *23* (4), 420.
1150. Itoh, N.; Xu, W.-C. Selective hydrogenation of phenol to cyclohexanone using palladium-based membranes as catalysts. Appl. Catal. A **1993**, *107*, 83.
1151. Itoh, N.; Xu, W.-C.; Haraya, K. Basic experimental study on palladium membrane reactors. J. Membr. Sci. **1992**, *66*, 149.
1152. Sun, H.; Leonard, J.J.; Shalit, H. Hydrogen Peroxide Production. US Patent 4,393,038, Jul. 12, 1983.
1153. Peureux, J.; Torres, M.; Mozzanega, H.; Giroir-Fendler, A.; Dalmon, J.-A. Nitrobenzene liquid-phase hydrogenation in a membrane reactor. Catal. Today **1995**, *25* (3–4), 409.
1154. Ilinich, O.M.; Cuperus, F.P.; van Gemert, R.W.; Gribov, E.N.; Nosova, L.V. Catalytic membrane in denitrification of water: A means to facilitate intraporous diffusion of reactants. Sep. Purif. Technol. **2000**, *21* (1–2), 55.
1155. Maier, W.F.; Ko, H.-C. Poison resistant catalysis with microporous catalyst membranes. Catal. Today **1995**, *25* (3–4), 429.
1156. Minet, R.G.; Tsotsis, T.T.; Champagnie, A.M. Process for Production of Ethylene from Ethane. US Patent 5,202,517, Apr. 13, 1993.
1157. Adris, A.M.; Lim, C.J.; Grace, J.R. The fluidized bed membrane reactor for steam methane reforming: Model verification and parametric study. Chem. Eng. Sci. **1997**, *52*, 1609.
1158. Labaton, I.J.; Harats, Y. Hydrogen Pump. US Patent 4,886,048, Dec. 12, 1989.
1159. Gobina, E.; Hughes, R. Reaction coupling in catalytic membrane reactors. Chem. Eng. Sci. **1996**, *51* (11), 3045.
1160. Itoh, N.; Govind, R. Development of a novel oxidative palladium membrane reactor. AIChE Symp. Ser. **1989**, *268* (85), 10.
1161. Sheintuch, M. Design of membranal dehydrogenation reactors: The fast reaction asymptote. Ind. Eng. Chem. Res. **1998**, *37* (3), 807.
1162. Balovnev, Y.A. Isotopic effect during hydrogen penetration through palladium. Phys. Met. Metallogr. **1978**, *45* (6), 167.
1163. Zhao, R.; Govind, R. Studies on palladium membrane reactor for dehydrogenation reaction. Sep. Sci. Technol. **1990**, *25* (13–15), 1473.
1164. Violante, V.; Drioli, E.; Basile, A. Catalytic ceramic membrane reactor

design for hydrogen separation from inert gas via oxidation. J. Membr. Sci. **1995**, *104*, 11.

1165. Hermann, C.; Quicker, P.; Dittmeyer, R. Mathematical simulation of catalytic dehydrogenation of ethylbenzene to styrene in a composite palladium membrane reactor. J. Membr. Sci. **1997**, *136*, 161.
1166. Hsu, C.; Buxbaum, R.E. Palladium-catalyzed oxidative diffusion for tritium extraction from breeder-blanket fluids at low concentrations. J. Nucl. Mater. **1986**, *141–143*, 238.
1167. Gobina, E.; Hughes, R. Reaction assisted hydrogen transport during catalytic dehydrogenation in a membrane reactor. Appl. Catal. A **1996**, *137* (1), 119.
1168. Itoh, N.; Govind, R. Combined oxidation and dehydrogenation in a palladium membrane reactor. Ind. Eng. Chem. Res. **1989**, *28*, 1554.
1169. Coppola, P.P. Hydrogen-pumping Apparatus of Laminated Construction. US Patent 3,630,690, Dec. 28, 1971.
1170. Wang, A.W.; Raich, B.A.; Johnson, B.K.; Foley, H.C. Coupled reaction–separation systems: Saturated hydrocarbon dehydrogenation with palladium membranes. Prepr.-Am. Chem. Soc., Div. Pet. Chem. **1992**, *37*, 743.
1171. Zaman, J.; Chakma, A. A simulation on the thermal decomposition of hydrogen sulfite in a membrane reaction. Int. J. Hydrogen Energy **1995**, *20* (1), 21.
1172. Raybold, T.M.; Huff, M.C. Catalytic oxidative dehydrogenation of isobutane in a Pd membrane reactor. Stud. Surf. Sci. Catal. **1997**, *110*, 501.
1173. Raybold, T.M.; Huff, M.C. Oxidation of isobutane over supported noble metal catalysts in a palladium membrane reactor. Catal. Today **2000**, *56* (1–3), 35.
1174. Wu, J.C.S.; Liu, P.K.T. Mathematical analysis on catalytic dehydrogenation of ethylebenzene using ceramic membranes. Ind. Eng. Chem. Res. **1992**, *31*, 322.
1175. Ali, J.K.; Rippin, D.W.T.; Baiker, A. Improving methylcyclohexane dehydrogenation with ex-situ hydrogen separation in a reactor-interstaged membrane system. Ind. Eng. Chem. Res. **1995**, *34* (9), 2940.
1176. Nagamoto, H.; Inoue, H. Analysis of mechanism of ethylene hydrogenation by hydrogen permeating palladium membrane. J. Chem. Eng. Jpn. **1981**, *14* (5), 377.
1177. Weyten, H.; Luyten, J.; Keizer, K.; Willems, L.; Leysen, R. Membrane performance: The key issues for dehydrogenation reactions in a catalytic membrane reactor. Catal. Today **2000**, *56* (1–3), 3.
1178. Ali, J.K.; Rippin, D.W.T. Comparing mono- and bimetallic noble-metal

catalysts in a catalytic membrane reactor for methylcyclohexane dehydrogenation. Ind. Eng. Chem. Res. **1995**, *34* (3), 722.

1179. Gobina, E. Inorganic membranes tackle oxo-alcohol synthesis gas production in a fluidised-bed reactor. Membr. Technol. **2000**, *2000*, 4.

1180. Adris, A.-E.M.; Grace, J.R.; Lim, C.J.; Elnashaie, S.S. Fluidized Bed Reaction System for Steam/Hydrocarbon Gas Reforming to Produce Hydrogen. US Patent 5,326,550, Jul. 5, 1994.

1181. Abdalla, B.K.; Elnashaie, S.S.E.H.; Alkhowaiter, S.; Elshishini, S.S. Intrinsic kinetics and industrial reactors modelling for the dehydrogenation of ethylbenzene to styrene on promoted iron oxide catalysts. Appl. Catal. A **1994**, *113*, 89.

1182. Buxbaum, R.E. Membrane reactor advantages for methanol reforming and similar reactions. Sep. Sci. Technol. **1999**, *34* (10), 2113.

1183. Hara, S.; Xu, W.-C.; Sakaki, K.; Itoh, N. Kinetics and hydrogen removal effect for methanol decomposition. Ind. Eng. Chem. Res. **1999**, *38* (2), 488.

1184. Lin, Y.-M.; Lee, G.-L.; Rei, M.-H. An integrated purification and production of hydrogen with a palladium membrane-catalytic reactor. Catal. Today **1998**, *44*, 343.

1185. Oklany, J.S.; Hou, K.; Hughes, R. A simulative comparison of dense and microporous membrane reactors for the steam reforming of methane. Appl. Catal., A **1998**, *170* (1), 13.

1186. Sheintuch, M.; Dessau, R.M. Observations, modeling and optimization of yield, selectivity and activity during dehydrogenation of isobutane and propane in a Pd membrane reactor. Chem. Eng. Sci. **1996**, *51* (4), 535.

1187. Lange, C.; Storck, S.; Tesche, B.; Maier, W.F. Selective hydrogenation reactions with a microporous membrane catalyst, prepared by sol-gel dip coating. J. Catal. **1998**, *175*, 280.

1188. Gokhale, Y.V.; Noble, R.D.; Falconer, J.L. Analysis of a membrane enclosed catalytic reactor for butane dehydrogenation. J. Membr. Sci. **1993**, *77*, 197.

1189. Gokhale, Y.V.; Noble, R.D.; Falconer, J.L. Effects of reactant loss and membrane selectivity on a dehydrogenation reaction in a membrane-enclosed catalytic reactor. J. Membr. Sci. **1995**, *105*, 63.

1190. Gobina, E.; Hou, K.; Hughes, R. Mathematical analysis of ethylbenzene dehydrogenation: Comparison of microporous and dense membrane systems. J. Membr. Sci. **1995**, *105*, 163.

1191. Reo, C.M.; Bernstein, L.A.; Lund, C.R.F. Defining conditions where the use of porous membrane reactors can be justified solely on the basis of improved yield. Chem. Eng. Sci. **1997**, *52* (18), 3075.

1192. Saracco, G.; Veldsink, J.W.; Versteeg, G.F.; van Swaaij, W.P.M. Catalytic combustion of propane in a membrane reactor with separate feed of reactants—II. Operation in presence of trans-membrane pressure gradients. Chem. Eng. Sci. **1995**, *50* (17), 2833.

1193. Gryaznov, V.M.; Smirnov, V.S.; Mischenko, A.P.; Aladyshev, S.I. Catalytic-reactor for Carrying Out Conjugate Chemical Reactions. US Patent 4,014,657, Mar. 29, 1977.

1194. Elnashaie, S.S.E.H.; Moustafa, T.M.; Alsoudani, T.; Elshishini, S.S. Modeling and basic characteristics of novel integrated dehydrogenation–hydrogenation membrane catalytic reactors. Comput. Chem. Eng. **2000**, *24*, 1293.

1195. Marigliano, G.; Barbieri, G.; Drioli, E. Effect of energy transport on a palladium-based membrane reactor for methane steam reforming process. Catal. Today **2001**, *67*, 85.

1196. Luk'yanov, B.N.; Ermilova, M.M.; Orekhova, N.V. Development of a kinetic model for the dehydrogenation of isoamylenes on a palladium–nickel membrane catalyst. Kinet. Catal. **1977**, *18* (3), 569.

1197. Khaldeev, G.V.; Petukhov, I.V.; Shcherban, M.G. Electrooxidation of the hypophosphite ion on a palladium electrode. Russ. J. Electrochem. (Elektrokhimiya) **2000**, *36* (9), 934.

1198. Orekhova, N.V.; Ermilova, M.M.; Smirnov, V.S.; Gryaznov, V.M. Effect of reaction products on dehydrogenation rate of isoamylenes on a membrane catalyst. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1976**, *11*, 2602.

1199. Johansson, M.; Ekedahl, L.-G. Hydrogen adsorbed on palladium during water formation studied with palladium membranes. Appl. Surf. Sci. **2001**, *173* (1–2), 122.

1200. Gorshkov, S.V.; Lin, G.I.; Rozovskii, A.Y. The mechanism of methanol dehydrogenation with methyl formate formation and the methods of process selectivity control. Kinet. Catal. **1999**, *40* (3), 334.

1201. Naito, S.; Amemiya, N. Noble selectivity change in the hydrogenation of CO over palladium membrane catalysts. Chem. Lett. **1996**, *10*, 893.

1202. Arai, M.; Wada, Y.; Nishiyama, Y. Desorption of hydrogen absorbed in a palladium film as induced by the adsorption of pyridine. J. Colloid Interface Sci. **1993**, *159*, 255.

1203. Karavanov, A.N.; Batirev, I.G. Calculation of reaction rate and selectivity of dehydrolinalool hydrogenation over Pd–Ru alloy membrane catalysts. Mendeleev Commun. **1993**, *2*, 62.

1204. Mishchenko, A.P.; Senina, E.V. Transformation of carbon tetrachloride on membrane catalysts. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1987**, *36* (7), 1541.

1205. Dannetun, H.; Lundstrom, I.; Petersson, L.G. Detection of hydrogen from the photodissociative splitting of water through hydrogen–oxygen separation over a thin Pd film. J. Appl. Phys. **1991**, *70* (1), 453.

1206. Ohkawa, K.; Noguchi, Y.; Nakayama, S.; Hashimoto, K. Electrochemical reduction of carbon dioxide on hydrogen-storing materials. Part 3. The effect of the absorption of hydrogen on the palladium electrodes modified with copper. J. Electroanal. Chem. **1994**, *367*, 165.
1207. Sokol'skii, D.V.; Nogerbekov, B.Y.; Gudeleva, N.N.; Kobets, N.V.; Mustafina, R.G. Diffusion of hydrogen through palladium-containing membrane catalysts. Russ. J. Phys. Chem. **1986**, *61* (1), 34.
1208. Itoh, N.; Xu, W.C.; Hara, S.; Sakaki, K. Electrochemical coupling of benzene hydrogenation and water electrolysis. Catal. Today **2000**, *56*, 307.
1209. Jerkiwicz, G.; Zolfaghari, A. Comparison of hydrogen electroadsorption from the electrolyte with hydrogen adsorption from the gas phase. J. Electrochem. Soc. **1996**, *143* (April), 1240.
1210. Amandusson, H.; Ekedahl, L.-G.; Dannetun, H. Isotopic study of ethanol dehydrogenation over a palladium membrane. J. Catal. **2000**, *195*, 376.
1211. Amandusson, H.; Ekedahl, L.-G.; Dannetun, H. Methanol-induced hydrogen permeation through a palladium membrane. Surf. Sci. **1999**, *442*, 199.
1212. Shirai, M.; Arai, M. Hydrogenation of furan with hydrogen atoms permeating through a palladium membrane. Langmuir **1999**, *15* (4), 1577.
1213. Shirai, M.; Pu, Y.; Arai, M.; Nishiyama, Y. Reactivity of permeating hydrogen with thiophene on a palladium membrane. Appl. Surf. Sci. **1998**, *126*, 99.
1214. Itoh, M.; Machida, K.; Adachi, G. Ammonia production characteristics of Ru/$Al_2O_3$ catalysts using hydrogen permeable membrane. Chem. Lett. **2000**, *10*, 1162.
1215. Nagamoto, H.; Inoue, H.T. The hydrogenation of 1,3-butadiene over a palladium membrane. Bull. Chem. Soc. Jpn. **1986**, *59*, 3935.
1216. Nagamoto, H.; Inoue, H. A reactor with catalytic membrane permeated by hydrogen. Chem. Eng. Commun. **1985**, *34*, 315.
1217. Arai, M.; Wada, Y.; Nishiyama, Y. Thiophene hydrodesulfurization by catalytic palladium membrane systems. Sekiyu Gakkaishi (J. Jpn. Pet. Inst.) **1993**, *36* (1), 44.
1218. Rupprechter, G.; Somorjai, G.A. Palladium-catalyzed hydrogenation without hydrogen: the hydrodechlorination of chlorofluorocarbons with solid state hydrogen over the palladium(111) crystal surface and its implications. Catal. Lett. **1997**, *48* (1,2), 17.
1219. Pick, M.A. The dependence of the hydrogen concentration in metals on the surface impurities. J. Nucl. Mater. **1987**, *145–147*, 297.

1220. Raymont, M.E.D. Make hydrogen from hydrogen sulfide. Hydrocarbon Process. **1975**, *54* (7), 139.

1221. Zubarev, Y.A.; Zelyaeva, E.A.; Mironovskaya, T.G.; Yagodovskii, V.D.; Gryaznov, V.M. Adsorption of ethylene and acetylene on palladium foil and films. Kinet. Catal. **1981**, *22* (5), 1005.

1222. Zubarev, Y.A.; Zelyaeva, E.A.; Moreno Fuken, R.; Yagodovskii, V.D.; Gryaznov, V.M. Study of the hydrogenation of ethylene and acetylene adsorbed on palladium foil by diffusing hydrogen. Kinet. Catal. **1983**, *24* (5), 990.

1223. Mischenko, A.P.; Gryaznov, V.M.; Smirnov, V.S.; Senina, E.D.; Parbuzina, I.L.; Roshan, N.R.; Polyakova, V.P.; Savitsky, E.M. Process for Producing Aniline with a Permselective Palladium and Ruthenium Catalyst. US Patent 4,179,470, Dec. 18, 1979.

1224. Mischenko, A.P.; Gryaznov, V.M.; Gakh, I.G.; Parbuzina, I.L.; Savitsky, E.M.; Polyakova, V.P.; Roshan, N.R. Method for Preparing 2,4-diaminolphenol or 2,4-dihydrochloride. US Patent 4,323,708, Apr. 6, 1982.

1225. Daley, S.P.; Utz, A.L.; Trautman, T.R.; Ceyer, S.T. Ethylene hydrogenation on Ni(111) by bulk hydrogen. J. Am. Chem. Soc. **1994**, *116* (13), 6001.

1226. Graifer, A.Y.; Koshcheev, A.P.; Myasnikov, I.A. Photostimulated hydrogen spillover in a semiconductor-palladium membrane system. Kinet. Catal. **1990**, *31* (6 (2)), 1315.

1227. Collins, J.P. Catalytic Decomposition of Ammonia in a Membrane Re2actor. Ph.D. Thesis; Oregon State University: Corvallis, Oregon, US, 1993.

1228. Collins, J.P.; Way, J.D. Catalytic decomposition of ammonia in a membrane reactor. Ind. Eng. Chem. Res. **1994**, *96*, 259.

1229. Gobina, E.N.; Oklany, J.S.; Hughes, R. Elimination of ammonia from coal gasification streams by using a catalytic membrane reactor. Ind. Eng. Chem. Res. **1995**, *34* (11), 3777.

1230. Collins, J.P.; Way, J.D.; Kraisuwansarn, N. A mathematical model of a catalytic membrane reactor for the decomposition of $NH_3$. J. Membr. Sci. **1993**, *77*, 265.

1231. Oertel, M.; Schmitz, J.; Weirich, W.; Jendryssek-Neumann, D.; Schulten, R. Steam reforming of natural gas with integrated hydrogen separation for hydrogen production. Chem.-Ing.-Tech. **1987**, *10* (4), 248.

1232. Nazarkina, E.G.; Kirichenkom, H.A. Improvement in the steam catalytic conversion of methane by hydrogen liberation via palladium membrane. Chem. Technol. Fuels Oils (Khim. Tekhnol. Topl. Masel) **1979**, *15* (3), 5.

1233. Ishihara, T.; Miyashita, Y.; Iseda, H.; Takita, Y. Decomposition of methane over Ni/$SiO_2$ catalysts with membrane reactor for the production of hydrogen. Chem. Lett. **1995**, 93.

1234. Batirev, I.G.; Karavanov, A.N.; Leiro, J.A. Surface segregation and catalytic properties of Pd–Ru alloys. Surf. Sci. **1993**, *289*, 357.

1235. Yoshitake, M.; Yoshihara, K. Surface segregation of substrate element on metal films in film/substrate combinations with Nb, Ti and Cu. Surf. Interface Anal. **1992**, *18*, 509.

1236. Rodina, A.A.; Gurevich, M.A.; Doronicheva, N.I. The interaction of hydrogen with certain palladium–gold and palladium–silver–gold alloys. Russ. J. Phys. Chem. **1971**, *45* (5), 621.

1237. Wood, B.J.; Wise, H. Surface composition of Pd–Au and Pd–Ag catalysts by Auger electron spectroscopy. Surf. Sci. **1975**, *52*, 151.

1238. Shapiro, E.S.; Telegina, N.S.; Gryaznov, V.M. Oscillations in the surface composition in Pt–Co alloys induced by CO chemisorption. Dokl. Phys. Chem. **1991**, *320* (4–6), 737.

1239. Shpiro, E.S.; Ustinova, T.S.; Smirnov, V.S.; Gryaznov, V.M.; Antoshin, G.V.; Minachev, K.M. The effect of various types of treatment on the surface layer composition in binary palladium alloys. Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR, Ser. Khim.) **1978**, *27* (4), 658.

1240. Kikuchi, E.; Uemiya, S.; Sato, N.; Inoue, H.; Ando, H.; Matsuda, T. Membrane reactor using microporous glass-supported thin film of palladium: 1) Application to the water gas shift reaction. Chem. Lett. **1989**, *3*, 489.

1241. Hou, K.; Fowles, M.; Hughes, R. The effect of hydrogen removal during methane steam reforming in membrane reactors in the presence of hydrogen sulphide. Catal. Today **2000**, *56* (1–3), 13.

1242. Hou, K.; Fowles, M.; Hughes, R. Potential catalyst deactivation due to hydrogen removal in a membrane reactor used for methane steam reforming. Chem. Eng. Sci. **1999**, *54*, 3783.

1243. Goltsov, V.A. Method for Preparation of Super-high Purity Hydrogen. US Patent 3,881,891, May 6, 1975.

1244. Amandusson, H.; Ekedahl, L.-G.; Dannetun, H. Alcohol dehydrogenation over Pd versus PdAg membranes. Appl. Catal. **2001**, *217*, 157.

1245. Emonts, B.; Bøgild Hansen, J.; Lægsgaard Jørgensen, S.; Höhlein, B.; Peters, R. Compact methanol reformer test for fuel-cell powered light-duty vehicles. J. Power Sources **1998**, *71*, 288.

1246. Roy, S.; Cox, B.G.; Adris, A.M.; Pruden, B.B. Economics and simulation of fluidized bed membrane reforming. Int. J. Hydrogen Energy **1998**, *23* (9), 745.

1247. Jiang, Z.; Wang, J.; Tong, H. In *Modeling Analysis of Membrane Reactor Process for Dehydrogenation of Ethylbenzene to Styrene*, Proc.

5th Intl. Conf. Inorganic Membr., Nagoya, Japan, June 22–26, 1998; 608.

1248. Becker, Y.L.; Dixon, A.G.; Moser, W.R.; Ma, Y.H. Modeling of ethylbenzene dehydrogenation in a catalytic membrane reactor. J. Membr. Sci. **1993**, *77*, 233.

1249. Tagawa, T.; Itoh, H.; Goto, S. In *Design of Palladium Membrane Reactor for Dehydrogenation of Ethylbenzene*, Proc. 5th Intl. Conf. Inorganic Membr., Nagoya, Japan, June 22–26, 1998; 342.

1250. Tiscareno-Lechuga, F.; Hill, C.G., Jr.; Anderson, M.A. Experimental studies of the non-oxidative dehydrogenation of ethylbenzene using a membrane reactor. Appl. Catal. A **1993**, *96*, 33.

1251. Yang, W.-S.; Wu, J.-C.; Lin, L.-W. Application of membrane reactor for dehydrogenation of ethylbenzene. Catal. Today **1995**, *25* (3–4), 315.

1252. She, Y.; Han, J.; Ma, Y.H. Palladium membrane reactor for the dehydrogenatation of ethylbenzene to styrene. Catal. Today **2001**, *67*, 43.

1253. Mahlman, J.D. Uncertainties in projections of human-caused climate warming. Science **1997**, *278*, 1416.

1254. The science of climate change. Science **2001**, *292*, 1261.

1255. Golunski, S. HotSpot$^{TM}$ fuel processor. Platinum Met. Rev. **1998**, *42* (1), 2.

1256. Ogden, J.; Steinbugler, M.M.; Kreutz, T.G. A comparison of hydrogen, methanol and gasoline as fuels for fuel cell vehicles: Implications for vehicle design and infrastructure development. J. Power Sources **1999**, *79* (2), 143.

1257. Liu, C.; Fan, Y.Y.; Liu, M.; Cong, H.T.; Cheng, H.M.; Dresselhaus, M.S. Hydrogen storage in single-walled carbon nanotubes at room temperature. Science **1999**, *286*, 1127.

1258. Choi, W.C.; Kim, J.D.; Woo, S.I. Modification of proton conducting membrane for reducing methanol crossover in a direct-methanol fuel cell. J. Power Sources **2001**, *96*, 411.

1259. Dohle, H. Fuel Cell with a Proton Conducting Electrolyte. WO Patent 9939398, Aug. 5, 1999.

1260. Smotkin, E.S.; Mallouk, T.E.; Ward, M.D.; Ley, K.L. Hybrid Electrolyte System. US Patent 5,846,669, Dec. 8, 1998.

1261. Edwards, N.; Ellis, S.R.; Frost, J.C.; Golunski, S.E.; van Keulen, A.N.F.; Lindewald, N.G.; Reinkingh, J.G. On-board hydrogen generation for transport applications: The HotSpot$^{TM}$ methanol processor. J. Power Sources **1998**, *71*, 123.

1262. Hoogers, G. Fuel cells: Power for the future. Phys. World Mag. **1998**, *11* (8), 31.

1263. Cicero, D.; Jarr, L.A. Application of ceramic membranes in advanced coal-based power generation systems. Sep. Sci. Technol. **1990**, *25* (13–15), 1455.

1264. Basile, A.; Paturzo, L. An experimental study of multilayered composite palladium membrane reactors for partial oxidation of methane to syngas. Catal. Today **2001**, *67*, 55.

1265. Nielsen, A.T.; Amandusson, H.; Bjorklund, R.; Dannetun, H.; Ejlertsson, J.; Ekedahl, L.-G.; Lundström, I.; Svensson, B.H. Hydrogen production from organic waste. Int. J. Hydrogen Energy **2001**, *26*, 547.

1266. Reed, T.B.; Lerner, R.M. Methanol: A versatile fuel for immediate use. Science **1973**, *182* (4119), 1299.

1267. Ahmed, S.; Kumar, R.; Krumpelt, M. Fuel processing for fuel cell power systems. Fuel Cells Bull. **1999**, *2* (12), 4.

1268. Brown, L.F. A comparative study of fuels for on-board hydrogen production for fuel-cell-powered automobiles. Int. J. Hydrogen Energy **2001**, *26*, 381.

1269. Dams, R.A.; Hayter, P.R.; Moore, S.C. In *The Processing of Alcohols, Hydrocarbons and Ethers to Produce Hydrogen for a PEMFC for Transportation Applications*, Proc. 32nd Intersociety Energy Conversion Eng. Conf., Honolulu, Hawaii, Jul. 27–Aug. 11997; AIChE 837.

1270. Fishtik, I.; Alexander, A.; Datta, R.; Geana, D. A thermodynamic analysis of hydrogen production by steam reforming of ethanol via response reactions. Int. J. Hydrogen Energy **2000**, *25*, 31.

1271. Amphlett, J.C.; Evans, M.J.; Mann, R.F.; Weir, R.D. Hydrogen production by the catalytic steam reforming of methanol. Part 2: Kinetics of methanol decomposition using Girdler G66B catalyst. Can. J. Chem. Eng. **1985**, *63*, 605.

1272. Amphlett, J.C.; Evans, M.J.; Jones, R.A.; Mann, R.F.; Weir, R.D. Hydrogen production by the catalytic steam reforming of methanol. Part 1: The thermodynamics. Can. J. Chem. Eng. **1981**, *59*, 720.

1273. Amphlett, J.C.; Creber, K.A.M.; Davis, J.M.; Mann, R.F.; Peppley, B.A.; Stokes, D.M. Hydrogen production by steam reforming of methanol for polymer electrolyte fuel cells. Int. J. Hydrogen Energy **1994**, *19* (2), 131.

1274. Amphlett, J.C.; Mann, R.F.; Weir, R.D. Hydrogen production by the catalytic steam reforming on methanol. Part 3: Kinetics of methanol decomposition using C18HC catalyst. Can. J. Chem. Eng. **1988**, *66*, 950.

1275. Gardner, T.J.; Sault, A.G.; Boespflug, E.P.; Brinker, C.J.; Tsai, A.C. Y.; Collins, J.P. *Hydrogen Production for Fuel Cells by Selective Dehydrogenation of Alkanes in Catalytic Membrane Reactors, SAND 99-0681*; Sandia National Laboratory: Albuquerque, New Mexico, US, 1999.

1276. Edlund, D. Versatile, low-cost and compact fuel processor for low-temperature fuel cells. Fuel Cells Bull. **1999**, *2* (14), 8.

1277. Murata, K.; Ito, N.; Hayakawa, T.; Suzuki, K.; Hamakawa, S. No deactivated production of hydrogen by pyrolysis of ethane over graphite-based catalysts using membrane-type reactors. Chem. Commun. **1999** (7), 573.

1278. Murata, K.; Hamakawa, S.; Suzuki, K.; Hayakawa, T. Hydrogen production by decomposition of hydrocarbons over Ni/Ca/carbon catalysts. Sekiyu Gakkaishi (J. Jpn. Pet. Inst.) **2000**, *43* (2), 162.

1279. Midilli, A.; Rzayev, P.; Olgun, H.; Ayhan, T. Solar hydrogen production from hazelnut shells. Int. J. Hydrogen Energy **2000**, *25*, 723.

1280. Ledjeff-Hey, K.; Formanski, V.; Kalk, T.; Roes, J. Compact hydrogen production systems for solid polymer fuel cells. J. Power Sources **1998**, *71*, 199.

1281. Amphlett, J.C.; Mann, R.F.; Peppeley, B.A.; Roberge, P.R.; Rodrigues, A.; Salvador, J.P. Simulation of a 250 kW diesel fuel processor/PEM fuel cell system. J. Power Sources **1998**, *71* (1–2), 179.

1282. Peppley, B.A.; Amphlett, J.C.; Kearns, L.M.; Mann, R.F.; Roberge, P.R. In *Hydrogen Generation for Fuel-Cell Power Systems by High-pressure Catalytic Methanol-steam Reforming*, Proc. 32nd Intersociety Energy Conversion Eng. Conf., Honolulu, Hawaii, July 27–August 1, 1997; AIChE 831.

1283. Lin, Y.-M.; Rei, M.-H. Process development for generating high purity hydrogen by using supported palladium membrane reactor as steam reformer. Int. J. Hydrogen Energy **2000**, *25*, 211.

1284. Höhlein, B.; Boe, M.; Bøgild-Hansen, J.; Bröckerhoff, P.; Colsman, G.; Emonts, B.; Menzer, R.; Riedel, E. Hydrogen from methanol for fuel cells in mobile systems: Development of a compact reformer. J. Power Sources **1996**, *61*, 143.

1285. Han, J.-N.; Kim, I.-S.; Choi, K.-S. Purifier-integrated methanol reformer for fuel cell vehicles. J. Power Sources **2000**, *86*, 223.

1286. Rampe, T.; Heinzel, A.; Vogel, B. Hydrogen generation from biogenic and fossil fuels by autothermal reforming. J. Power Sources **2000**, *86*, 536.

1287. Gubler, L.; Scherer, G.G.; Wokaun, A.; Newson, E.; Truong, T.B.; von Roth, F. *Lab Scale Link-up of a Methanol Fuel Processor with a Polymer Electrolyte Fuel Cell (PEFC). Paul Scherrer Institute Scientific Report. Volume V: General Energy, ETDE-CH-0001 or DE20063988*; Paul Scherrer Institute, 1999.

1288. Edlund, D.J. Steam Reformer with Internal Hydrogen Purification. US Patent 5,861,137, Jan. 19, 1999.

1289. Isomura, M.; Soma, T.; Takahashi, T. Process for Production of High-purity Hydrogen. US Patent 5,741,474, Apr. 21, 1998.

1290. Shirasaki, Y.; Gondaira, M.; Ohta, Y.; Uchida, H.; Kuroda, K.; Uchida, T.; Fujimoto, Y.; Makihara, H.; Ohta, S.; Kobayashi, K. Hydrogen Producing Apparatus. US Patent 5,639,431, Jun. 17, 1997.

1291. Marianowski, L.G.; Fleming, D.K. Hydrogen Forming Reaction Process. US Patent 4,810,485, Mar. 7, 1989.

1292. Setzer, H.J.; Eggen, C.W. Method for Catalytically Reforming Hydrogen-containing Carbonaceous Feedstocks by Simultaneous Abstractions Through a Membrane Selectively Permeable to Hydrogen. US Patent 3,450,500, Jun. 17, 1969.

1293. Weirich, W.; Barnert, H.; Oertel, M.; Schulten, R. Process and Apparatus for Conversion of Water Vapor with Coal or Hydrocarbon into a Product Gas. US Patent 4,713,234, Dec. 15, 1987.

1294. Epp, D.G.; Baumert, R.M. Integrated Fuel Cell Electric Power Generation System for Submarine Applications. US Patent 6,063,515, May 16, 2000.

1295. LaPierre, R.; Partridge, R.D. Method and Sytsem for Supplying Hydrogen for Use in Fuel Cells. WO Patent 9965097, Dec. 16, 1999.

1296. Edwards, N.; VanKeulen, A.N.J. Hydrogen Generator. WO Patent 9925649, May 27, 1999.

1297. Bloomfield, D.P. Fuel Cell Power Plant with Electrochemical Autothermal Reformer. WO Patent 9904443, Jan. 28, 1999.

1298. Soma, T.; Takahashi, T.; Isomura, M. Method for Removing Carbon Monoxide from Reformed Gas. US Patent 5,612,012, Mar. 18, 1997.

1299. Edlund, D.J.; Pledger, W.A. Hydrogen Producing Fuel Processing System. US Patent 6,221,117, 2001.

1300. Buxbaum, R.E. High Temperature Gas Purification System. US Patent 5,888,273, 1999.

1301. Willms, R.S.; Birdsell, S.A. Apparatus and Method for Simultaneous Recovery of Hydrogen from Water and from Hydrocarbons. WO Patent 9934898, 1999.

1302. Birdsell, S.A.; Willms, R.S. Hydrogen Generation from Reforming Organic Molecules using a Palladium Membrane Reactor. WO Patent 9961368, Dec. 2, 1999.

1303. Penzhorn, R.-D.; Yoshida, H. Process for Cleaning the Exhaust Gas of a Fusion Reactor. US Patent 4,875,945, Oct. 24, 1989.

1304. Farrauto, R.J. The generation of hydrogen for the solid polymer membrane fuel cell. C. R. Acad. Sci., Ser. IIc: Chim. **2000**, *7* (3), 573.

1305. Arvindan, N.S.; Rajesh, B.; Madhivanan, M.; Pattabiraman, R. Hydrogen generation from natural gas and methanol for use in electrochemical energy conversion systems (fuel cell). Indian J. Eng. Mater. Sci. **1999**, *6*, 73.

1306. Meek, J.; Baker, B.S. Hydrogen from Natural Gas for Fuel Cells. In *Advances in Chemistry Series*; Young, G.J., Linden, H.R., Eds.; American Chem. Soc.: New York, 1965; Vol. 47, 221.

1307. Amphlett, J.C.; Mann, R.F.; Peppley, B.A. On board hydrogen purification for steam reformation/PEM fuel cell vehicle power plants. Int. J. Hydrogen Energy **1996**, *21* (8), 673.

1308. Gorshkov, S.V.; Lin, G.I.; Rozovskii, A.Y.; Serov, Y.M.; Uhm, S.J. Hydrogen diffusion through a Pd–Ru membrane in the course of methanol dehydrogenation to methyl formate on a copper-containing catalyst. Kinet. Catal. **1999**, *40* (1), 93.

1309. Amano, M.; Nishimura, C.; Komaki, M. Effects of high concentration CO and $CO_2$ on hydrogen permeation through the palladium membrane. Mater. Trans., JIM **1990**, *31* (5), 404.

1310. Rudbeck, P.; Aasberg-Petersen, K.; Lægsgaard Jørgensen, S.; Højlund Nielsen, P.E. Process for the Generation of Electrical Power. US Patent 5,705,916, Jan. 6, 1998.

1311. Ishutin, V.V.; Mekhedov, B.N.; Sukhotin, L.N. Separation of hydrogen and tritium on a palladium filter. Russ. J. Phys. Chem. **1972**, *46* (10), 1516.

1312. Charalambus, S.; Goebel, K. Enrichment of tritium by diffusion through palladium. Z. Naturforsch., A: Phys. Sci. **1965**, *20*, 1085.

1313. Chu, W. Hydrogen purifiers go to Savannah River site to process tritium. Radioact. Radiochem. **1996**, *7* (4), 45.

1314. Clark, E.A.; Dauchess, D.A.; Heung, L.K.; Rabun, R.L.; Motyka, T. Experience with palladium diffusers in tritium processing. Fusion Technol. **1995**, *28*, 566.

1315. Yoshida, H.; Konishi, S.; Naruse, Y. Preliminary design of a fusion reactor fuel cleanup system by the palladium–alloy membrane method. Nucl. Technol./Fusion **1983**, *3*, 471.

1316. Kawano, T.; Sakuma, Y.; Kabutomori, T.; Shibuya, M. Development of a tritium cleanup system for a large helical device using nonvolatile getter materials. Fusion Technol. **2000**, *37*, 62.

1317. Horsley, G.W. *On The Possibility of Removing Hydrogen from the Dragon Coolant by Diffusion Through a Palladium Membrane, NP-9743*; Atomic Energy Establishment: Winfrith, England, 1960.

1318. Kamei, H.; Ohno, M. Removal of Hydrogen from Liquid Sodium. US Patent 3,795,087, Mar. 5, 1974.

1319. Konishi, S.; Inoue, M.; Hayashi, T.; O'hira, S.; Watanabe, T.; Okuno, K.; Naruse, Y.; Barnes, J.W.; Bartlit, J.R.; Andrerson, J.L. Early experiments of JAERI fuel cleanup system at the tritium systems test assembly. Fusion Eng. Des. **1991**, *18*, 33.

1320. Konishi, S.; Yoshida, H.; Naruse, Y. Analysis and design of palladium diffuser for fusion reactor fuel cleanup system. At. Energy Soc. Jpn. J. **1982**, *24* (12), 973.
1321. Ali-Khan, I.; Dietz, K.-J.; Waelbroeck, F.; Wienhold, P. Device Utilized for Separation of Hydrogen Isotopes from a Gas Mixture for Separation of Isotopes Contained in a Hydrogen Isotope Mixture. US Patent 4,494,965, 1985.
1322. Penzhorn, R.-D.; Murdoch, D.; Haange, R. Recent results on vacuum pumping and fuel clean-up. Fusion Eng. Des. **1997**, *36*, 75.
1323. Hickam, W.M.; Witkowski, R.E.; Berkey, E. Diffusion-type Hydrogen Meter. US Patent 3,977,232, Aug. 31, 1976.
1324. Watson, C.C. Hydrogen Meter. US Patent 2,456,163, Dec. 14, 1948.
1325. Lucero, D.P. Electrochemical Cell with Hydrogen Permeable Barrier. US Patent 3,468,781, Sep. 23, 1969.
1326. Rzhanov, A.E.; Serov, Y.M.; Terent'ev, A.A.; Filippov, V.I.; Goncharov, V.Y. Hydrogen extraction from industrial media by a palladium–ruthenium(VI) membrane. J. Anal. Chem. USSR (Zh. Anal. Khim.) **1990**, *45* (9), 1335.
1327. Takagi, I.; Toyoda, K.; Katayama, M.; Fujita, H.; Higashi, K. Experiment on atomic hydrogen reflection by use of a permeation probe. J. Nucl. Mater. **1998**, *258–263*, 1082.
1328. Kohler, M. Engineering and design of fast reactors. Philos. Trans. R. Soc. London, Ser. A **1990**, *331* (1619), 301.
1329. Lawrence, S.C., Jr.; Picard, J.C.; Reich, R. A system for monitoring hydrogen–metal reaction kinetics. J. Less-Common Met. **1976**, *49*, 241.
1330. Chaplanov, V.; Filipopov, V.; Rzhanov, A.; Terentjev, A.; Yakimov, S. System to detect hydrogen in water. Sens. Actuators, B **1991**, *5* (1–4), 185.
1331. Serra, E.; Kemali, M.; Perujo, A.; Ross, D.K. Hydrogen and deuterium in Pd-25 Pct Ag alloy: Permeation, diffusion, solubilization, and surface reaction. Metall. Mater. Trans. A **1998**, *29A*, 1023.
1332. Bellanger, G.; Rameau, J.J. Tritium adsorption and diffusion of 25% silver palladium cathodic membranes for water processing. Fusion Technol. **1997**, *31*, 185.
1333. Lässer, R.; Schober, T. Some aspects of tritium storage in hydrogen storage materials. Mater. Sci. Forum **1988**, *31*, 39.
1334. Santandrea, R.P.; Behrens, R.G. A review of the thermodynamics and phase relationships in the palladium–hydrogen, palladium–deuterium and palladium–tritium systems. High Temp. Mates. Processes **1986**, *7* (2–3), 149.

1335. Wicke, E. Isotope effects in palladium–hydrogen systems. Platinum Met. Rev. **1971**, *15* (4), 144.

1336. Carstens, D.H.W.; David, W.R. *Equilibrium Pressure Measurements in the Beta Region of Palladium Protide and Palladium Deuteride,* LA-11456-MS; Los Alamos National Laboratory: 1989.

1337. Carstens, D.H.W.; Encinias, P.D. *Hydrogen Isotopic Exchange over Palladium Metal, LA-UR-90-1762*; Los Alamos National Laboratory, 1990.

1338. Chang, C.P.; Wu, J.K.; Yao, Y.D.; Wang, C.W.; Lin, E.K. Hydrogen and deuterium in palladium. Int. J. Hydrogen Energy **1991**, *16* (7), 491.

1339. Powell, G.L.; Lever, W.E. The solubility of H, D, and T in $Pd_{(1-Z)}Ag_Z$ Alloys ($Z = 0$ to 1). Z. Phys. Chem. N.F. **1989**, *163*, 47.

1340. Lässer, R.; Powell, G.L. Solubility of protium, deuterium and tritium in palladium–silver alloys at low hydrogen concentrations. J. Less-Common Met. **1987**, *130*, 387.

1341. Birnbaum, H.K.; Wert, C.A. Diffusion of hydrogen in metals. Ber. Bunsen-Ges. **1972**, *76* (8), 806.

1342. Lewis, F.A. The hydrides of palladium and palladium alloys: A review of recent researches. Platinum Met. Rev. **1960**, *4* (4), 132.

1343. Yasumatsu, T.; Watanabe, K.; Matsuyama, M. Thermodynamic properties of hydrogen isotope in Pd–Pt and Pd–Ni alloys. Annu. Rep. of Hydrogen Isot. Res. Cent., Toyama Univ. (Toyama Daigaku Suiso Doitai Kino Kenkyu Senta Kenkyu Hokoku) **1999**, *18*, 81.

1344. Watanabe, K.; Matsuyama, M.; Kobayashi, T.; Shu, W.M. Hydrogen isotope separation by gas chromatography using Pd–Pt alloy. Fusion Eng. Des. **1998**, *39–40*, 1001.

1345. Tosti, S.; Violante, V. Numerical approach for a study of the hydrogen isotopes separation by palladium alloy membranes. Fusion Eng. Des. **1998**, *43*, 93.

1346. Suzuki, Y.; Kimura, S. Separation and concentration of hydrogen isotopes by a palladium alloy membrane. Nucl. Tech. **1993**, *103*, 93.

1347. Suzuki, Y.; Kimura, S. Separation and concentration of hydrogen isotopes by palladium–alloy membrane. J. At. Energy Soc. Jpn. **1984**, *26* (9), 802.

1348. Sicking, G. Isotope effects in metal–hydrogen systems. J. Less-Common Met. **1984**, *101*, 169.

1349. Evans, J.; Harris, I.R.; Ross, D.K. A proposed method of hydrogen isotope separation using palladium alloy membranes. J. Less-Common Met. **1983**, *89*, 407.

1350. Rutherford, W.M. Separation of hydrogen isotopes. Mater. Sci. Forum **1988**, *31*, 19.

1351. Tanaka, S.; Kiyose, R. Isotope separation of hydrogen and deuterium by permeation through palladium membrane. J. Nucl. Sci. Technol. **1979**, *16* (12), 923.

1352. Konishi, S.; Yoshida, H.; Ohno, H.; Naruse, Y.; Coffin, D.O.; Walthers, C.R.; Binning, K.E. Experiments on a ceramic electrolysis cell and a palladium diffuser at the tritium systems test assembly. Fusion Technol. **1985**, *8*, 2042.

1353. Penzhorn, R.-D.; Berndt, U.; Kirste, E.; Hellriegel, W.; Jung, W.; Pejsa, R.; Romer, O. Long-term permeator experiment PETRA at the tritium laboratory Karlsruhe: Commissioning tests with tritium. Fusion Technol. **1995**, *28*, 723.

1354. Ortiz, T.M.; Meyer, B.A.; Razani, A. Empirical correlation of equilibrium separation factors in the $Pd-H_2/D_2$ system with temperature and composition. J. Chem. Eng. Data **2000**, *45* (1), 120.

1355. Botter, F. Thermodynamic isotopic effects in palladium and Pd–Pt alloy. J. Less-Common Met. **1976**, *49* (1–2) 111–122.

1356. Andreev, B.M.; Domanov, M.M. Temperature variation of the separation factor in the protium–tritium and deuterium–tritium systems on dissolution of hydrogen in palladium. Russ. J. Phys. Chem. **1975**, *49* (5), 734.

1357. Andreev, B.M.; Polevoi, A.S.; Perevezentsev, A.N. Effect of isotopic concentration on the separation coefficient of H–T, H–D, and D–T mixtures in the hydrogen–palladium system. Soc. At. Energ. (At. Energ.) **1978**, *45* (1), 710.

1358. Andreev, B.M.; Sicking, G.H. Hydrogen equilibrium separation factors in metal/hydrogen systems, a synopsis on the basis of the localized harmonic oscillator model. Ber. Bunsen-Ges. **1987**, *91*, 177.

1359. Nishikawa, M.; Shiraishi, T.; Murakami, K. Solubility and separation factor of protium–deuterium binary component system in palladium. J. Nucl. Sci. Technol. **1996**, *33* (6), 504.

1360. Gol'tsov, V.A.; Demin, V.B.; Vykhodets, V.B.; Kagan, G.Y.; Gel'd, P.V. Diffusion, penetration and solubility of hydrogen and deuterium in palladium. Phys. Met. Metallogr. **1970**, *29* (6), 195.

1361. Guilinger, T.R.; Kelly, M.J.; Knapp, J.A.; Walsh, D.S.; Doyle, B.L. Ion beam measurement of deuterium in palladium and calculation of hydrogen isotope separation factors. J. Electrochem. Soc. **1991**, *138* (8), L26.

1362. Skorodumov, B.G.; Serebryakov, V.N.; Ulanov, V.G.; Zhukovska, E.V.; Zhukovsky, O.A. Hydrogen and deuterium mass transfer and separation during hydriding–dehydriding of palladium studied by the NERD method. Int. J. Hydrogen Energy **1996**, *21* (11/12), 961.

1363. Thiébaut, S.; Décamps, B.; Pénisson, J.M.; Limacher, B.; Percheron-

Guégan, A. TEM study of the aging of palladium-based alloys during tritium storage. J. Nucl. Mater. **2000**, *277*, 217.

1364. Carlson, R.V.; Binning, K.E.; Konishi, S.; Yoshida, H.; Naruse, Y. In *Results of Experiments on Ceramic Electrolysis Cells and Palladium Diffusers for Application to Fusion Reactor Fuel Cleanup Systems*, Proc. 12th Symp. Fusion Eng., Monterey, California, US, 1987; IEEE: New York, 732.

1365. Klevtsov, V.G.; Boitsov, I.E.; Vedeneev, A.I.; Glagolev, M.V.; Lobanov, V.N.; Malkov, I.L.; Pimanikhin, S.A.; Stengach, A.V. The impact of tritium on the structure and properties of Pd-membranes. Fusion Eng. Des. **2000**, *49–50*, 873.

1366. Yoshida, H.; Kveton, O.; Koonce, J.; Holland, D.; Haange, R. Status of the ITER tritium plant design. Fusion Eng. Des. **1998**, *39–40*, 875.

1367. Penzhorn, R.-D.; Anderson, J.; Haange, R.; Hircq, B.; Meikle, A.; Naruse, Y. Technology and component development for a closed tritium cycle. Fusion Eng. Des. **1991**, *16*, 141.

1368. Glugla, M.; Murdoch, D.K.; Geibler, H.; Herrmann, P.; Kraemer, R.; Le, T.L. Design of a catalytic exhaust clean-up unit for ITER. Fusion Eng. Des. **1998**, *39–40*, 893.

1369. Konishi, S.; Hara, M.; Okuno, K. Versatile fuel cleanup system based on palladium permeation and vapor electrolysis. Fusion Technol. **1995**, *28*, 652.

1370. Busigin, A.; Sood, S.K.; Kalyanam, K.M. Process and Apparatus for Tritium Recovery. US Patent 5,154,878, Oct. 13, 1992.

1371. DeLong, B.W.; Burkinshaw, J.R. Gas Separation. US Patent 4,732,583, Mar. 22, 1988.

1372. Pigarov, A.Y.; Pistunovich, V.I.; Livshits, A.I. On gas pumping by using superpermeable membrane in ITER. J. Nucl. Mater. **1992**, *196–198*, 1121.

1373. Pistunovich, V.I.; Pigarov, A.Y.; Busnyuk, A.O.; Livshits, A.I.; Notkin, M.E.; Samartsev, A.A.; Borisenko, K.L.; Darmogray, V.V.; Ershov, B.D.; Filippova, L.V.; Mudugin, B.G.; Odintsov, V.N.; Saksagansky, G.L.; Serebrennikov, D.V. Membrane pumping technology for helium and hydrogen isotope separation in the fusion reactor. Fusion Eng. Des. **1995**, *28*, 336.

1374. Notkin, M.E. Interaction of hydrogen atoms with a palladium membrane. Sov. Phys. Tech. Phys. (Zh. Tekh. Fiz.) **1979**, *24* (9), 1089.

1375. Livshits, A.I.; Sube, F.; Solovyev, M.N.; Notkin, M.E.; Bacal, M. Plasma driven superpermeation of hydrogen through group Va metals. J. Appl. Phys. **1998**, *84* (5), 2558.

1376. Park, J.; Bennett, T.; Schwarzmann, J.; Cohen, S.A. Permeation of hydrogen through palladium. J. Nucl. Mater. **1995**, *220–222*, 827.

1377. Kapitanskii, V.R.; Livshits, A.I.; Metter, I.M.; Notkin, M.E. Interaction of a palladium membrane with quasiequilibrium atomic hydrogen. Sov. Phys. Tech. Phys. (Zh. Tekh. Fiz.) **1976**, *21* (5), 602.

1378. Livshits, A.I.; Notkin, M.E.; Samartsev, A.A. Physico-chemical origin of superpermeability-large-scale effects of surface chemistry on ''hot'' hydrogen permeation and absorption in metals. J. Nucl. Mater. **1990**, *170*, 79.

1379. Livshits, A.I. Superpermeability of solid membranes and gas evacuation. Part I. Theory. Vacuum **1979**, *29* (3), 103.

1380. Livshits, A.I. Superpermeability of solid membranes and gas evacuation. Part II. Permeation of hydrogen through a palladium membrane under different gas and membrane boundary conditions. Vacuum **1979**, *29* (3), 113.

1381. Livshits, A.I.; Notkin, M.E.; Pistunovich, V.I.; Bacal, M.; Busnyuk, A.O. Superpermeability: Critical points for applications in fusion. J. Nucl. Mater. **1995**, *220–222*, 259.

1382. Livshits, A.I.; Metter, I.M.; Samartsev, A.A. Interaction of a deuterium atomic beam with a palladium membrane. Sov. Phys. Tech. Phys. (Zh. Tekh. Fiz.) **1976**, *21* (7), 848.

1383. Nagasaki, T.; Ohno, H. Steady-state hydrogen transport in a metal membrane exposed to hydrogen gas and/or a hydrogen ion beam: Reexamination of transport regime and synergistic effects. J. Vac. Sci. Technol., A **1993**, *11* (3), 588.

1384. Sharapov, V.M. Impact of low-energy ion irradiation on desorption during hydrogen penetration through metals. Bull. Russ. Acad. Sci. Phys. **2000**, *64* (4), 588.

1385. Busnyuk, A.; Nakamura, Y.; Nakahara, Y.; Suzuki, H.; Ohyabu, N.; Livshits, A.I. Membrane bias effects on plasma-driven permeation of hydrogen through niobium membrane. J. Nucl. Mater. **2001**, *290–293*, 57.

1386. Nakahara, Y.; Nakamura, Y.; Ohyabu, N.; Suzuki, H.; Busnyuk, A.; Alimov, V. Superpermeable membrane for particle control in divertor: The effect of impurity deposition. Fusion Eng. Des. **2000**, *21–52*, 243.

1387. Violante, V.; Bettinali, L.; Bimbi, L.; Drioli, E. Ceramic Catalytic Membrane Reactor for the Separation of Hydrogen and/or Isotopes thereof from Fluid Feeds. US Patent 5,366,712, Nov. 22, 1994.

1388. Violante, V.; Basile, A.; Drioli, E. Composite catalytic membrane reactor analysis for the water gas shift reaction in the tritium fusion fuel cycle. Fusion Eng. Des. **1995**, *30*, 217.

1389. Birdsell, S.A.; Willms, R.S. *Tritium Recovery from Tritiated Water with a Two-stage Palladium Membrane Reactor, DE97004769*; Los Alamos National Laboratory: Los Alamos, New Mexico, US, 1997.

1390. Birdsell, S.A.; Willms, S.; Wilhelm, R.C. Ultra-high tritium decontamination of simulated fusion fuel exhaust using a 2-stage palladium membrane reactor. Fusion Technol. **1996**, *30*, 905.

1391. Separation of hydrogen isotopes. Platinum Met. Rev. **1957**, *1* (1), 49.

1392. Quakernaat, J. Hydrogen in a global long-term perspective. Int. J. Hydrogen Energy **1995**, *20* (6), 485.

1393. Bockris, J.O.M. Hydrogen economy. Environment **1971**, *13* (10), 51.

1394. Lewis, F.A.Q. Platinum metals involvement in the hydrogen economy. Platinum Met. Rev. **1997**, *41* (4), 163.

1395. Lovins, A.B.; Williams, B.D. *A Strategy for the Hydrogen Transition*; Rocky Mountain Institute: Snowmass, Colorado, US, 1999.

1396. Matsui, K. Global demand growth of power generation, input choices and supply security. J. Energy **1998**, *19* (2), 93.

1397. Newson, E.; Haueter, T.; Hottinger, P.; von Roth, F.; Scherer, G.W.H.; Schucan, T.H. Seasonal storage of hydrogen in stationary systems with liquid organic hydrides. Int. J. Hydrogen Energy **1998**, *23* (10), 905.

1398. Shakhbazov, S.D.; Rzaev, P.F. Thermal calculations for the reactor of a solar-power unit to produce hydrogen by thermolysis of water. Appl. Sol. Energy (Geliotekhnika) **1978**, *14* (2), 69.

1399. Bakirov, M.Y.; Rzaev, P.F.; Akhmedov, Z.G.; Velieva, B.A. A diffusion cell with palladium membrane for separation of hydrogen-containing mixtures in a solar furnace. Appl. Sol. Energy (Geliotekhnika) **1979**, *15* (5), 48.

1400. Wallman, P.H.; Thorsness, C.B.; Winter, J.D. Hydrogen production from wastes. Energy **1998**, *23* (4), 271.

1401. Arai, M.; Yamada, K.; Nishiyama, Y. Evolution and separation of hydrogen in the photolysis of water using titania-coated catalytic palladium membrane reactor. J. Chem. Eng. Jpn. **1992**, *25* (6), 761.

1402. Nishiguchi, H.; Fukunaga, A.; Miyashita, Y.; Ishihara, T.; Takita, Y. Reduction of carbon dioxide to graphite carbon via methane by catalytic fixation with membrane reactor. Stud. Surf. Sci. Catal. **1998**, *114*, 147.

1403. Kokugan, T.; Trianto, A.; Takeda, H. Dehydrogenation of pure cyclohexane in the membrane reactor and prediction of conversion by pseudo equilibrium model. J. Chem. Eng. Jpn. **1998**, *31* (4), 596.

1404. Aristov, Y.I.; Parmon, V.N.; Cacciola, G.; Giordano, N. High-temperature chemical heat pump based on reversible catalytic reactions of cyclohexane–dehydrogenation/benzene–hydrogenation: Comparison of the potentialities of different flow diagrams. Int. J. Energy Res. **1993**, *17*, 293.

1405. Cacciola, G.; Aristov, Y.I.; Restuccia, G.; Parmon, V.N. Influence of hydrogen-permeable membranes upon the effiency of the high-temperature chemical heat pumps based on cyclohexane dehydrogenation–benzene hydrogenation reactions. Int. J. Hydrogen Energy **1993**, *18* (8), 673.

1406. Hayes, J.M. Isotope-ratio-monitoring Gas Chromatography-mass Spectrometry Apparatus and Method. US Patent 5,012,052, Apr. 30, 1991.
1407. Lucero, D.P.; Haley, F.C. Sample enrichment techniques for a gas chromatograph/mass spectrometer analysis system. J. Gas Chromatogr. **1968**, *6*, 477.
1408. Lanzerstorfer, C.; Puxbaum, H. The palladium/silver membrane focusing injector—a new inlet system for thermal desorption capillary gas chromatography. Fresenius' J. Anal. Chem. **1991**, *339* (4), 223.
1409. Kanunnikova, E.V.; Gryaznov, V.M.; Yanovskii, S.M.; Pavlova, L.F.; Zhukhovitskii, A.A. The application of columns with semipermeable walls in chromatography. Ind. Lab. (Zavod. Lab.) **1976**, *42* (1), 18.
1410. Ford, T.E.; Searson, P.C.; Harris, T.; Mitchell, R. Investigation of microbiologically produced hydrogen permeation through palladium. J. Electrochem. Soc. **1990**, *137* (4), 1175.
1411. Paiva, A.L.; Malcata, F.X. Does thermodynamics improve processing when chemical reaction is integrated with physical separation in binary ideal mixtures? Chem. Eng. Sci. **1997**, *52* (3), 449.