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Abstract

Colorado School of Mines (CSM) developed high temperature, hydrogen permeable membranes that contain no platinum group metals with the goal of separating hydrogen from gas mixtures representative of gasification of carbon feedstocks such as coal or biomass in order to meet DOE NETL 2015 hydrogen membrane performance targets. We employed a dual synthesis strategy centered on transition metal carbides. In the first approach, novel, high temperature, surface diffusion membranes based on nanoporous Mo_2C were fabricated on ceramic supports. These were produced in a two step process that consisted of molybdenum oxide deposition followed by thermal carburization. Our best Mo_2C surface diffusion membrane achieved a pure hydrogen flux of 367 SCFH/ft^2 at a feed pressure of only 20 psig. The highest H_2/N_2 selectivity obtained with this approach was 4.9. A transport model using “dusty gas” theory was derived to describe the hydrogen transport in the Mo_2C coated, surface diffusion membranes. The second class of membranes developed were dense metal foils of BCC metals such as vanadium coated with thin ($< 60 \text{ nm}$) Mo_2C catalyst layers. We have fabricated a $\text{Mo}_2\text{C}/\text{V}$ composite membrane that in pure gas testing delivered a H_2 flux of **238 SCFH/ft^2 at 600°C and 100 psig** , with no detectable He permeance. This exceeds the 2010 DOE Target flux. This flux is 2.8 times that of pure Pd at the same membrane thickness and test conditions and over 79% of the 2015 flux target. In mixed gas testing we achieved a permeate purity of $\geq 99.99\%$, satisfying the permeate purity milestone, but the hydrogen permeance was low, $\sim 0.2 \text{ SCFH/ft}^2\text{.psi}$. However, during testing of a Mo_2C coated Pd alloy membrane with DOE 1 feed gas mixture a hydrogen permeance of $>2 \text{ SCFH/ft}^2\text{.psi}$ was obtained which was stable during the entire test, meeting the permeance associated with the 2010 DOE target flux. Lastly, the $\text{Mo}_2\text{C}/\text{V}$ composite membranes were shown to be stable for at least 168 hours = one week, including cycling at high temperature and alternating He/H_2 exposure.

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Executive Summary

Colorado School of Mines (CSM) developed high temperature, hydrogen permeable membranes that contain no platinum group metals with the goal of separating hydrogen from gas mixtures representative of gasification of carbon feedstocks such as coal or biomass in order to meet DOE NETL 2015 hydrogen membrane performance targets. We employed a dual synthesis strategy centered on transition metal carbides. In the first approach novel, high temperature, surface diffusion membranes based on nanoporous Mo_2C were fabricated on porous, planar and tubular substrates. These were produced in a two-step process that consisted of molybdenum oxide deposition followed by thermal carburization. Our best Mo_2C surface diffusion membrane achieved a pure hydrogen flux of 367 SCFH/ft^2 at a feed pressure of only 20 psig. The highest H_2/N_2 selectivity obtained with this approach was 4.9. A transport model using “dusty gas” theory was derived to describe the hydrogen transport in the Mo_2C coated, surface diffusion membranes.

The second class of membranes developed were dense metal foils of BCC metals such as vanadium coated with thin ($< 60 \text{ nm}$) Mo_2C catalyst layers to dissociate the molecular hydrogen. We have fabricated a $\text{Mo}_2\text{C}/\text{V}$ composite membrane that in pure gas testing delivered a H_2 flux of **238 SCFH/ft^2 at 600°C and 100 psig** , with no detectable He permeance. This exceeds the 2010 DOE Target flux of 200 SCFH/ft^2 . This flux is 2.8 times that of pure Pd at the same membrane thickness and test temperature and over 79% of the 2015 flux target of 300 SCFH/ft^2 .

The Colorado School of Mines was awarded U. S. patent #8,623,121 B2 entitled, “Stable Catalyst Layers for Hydrogen Permeable Composite Membranes,” covering these novel membrane synthesis methods. This patent can be found in Appendix A of this report.

In mixed gas testing with Mo_2C coated V foil membranes, we achieved a permeate purity of $\geq 99.99\%$, satisfying the permeate purity milestone, but the hydrogen permeance was low, $\sim 0.2 \text{ SCFH/ft}^2\cdot\text{psi}$. In these initial tests, we hypothesized that the flux was limited either by concentration polarization in the membrane test cell and/or competitive adsorption from gas mixture components including steam or carbon monoxide. Further mixed gas permeation testing with a Mo_2C coated, Pd alloy, tubular membrane with the DOE 1 feed gas mixture yielded a hydrogen permeance of $> 2 \text{ SCFH/ft}^2\cdot\text{psi}$ which was stable during the entire test. The hydrogen permeate purity was $> 99.8\%$ for all mixed gas test conditions. The permeance (flux/driving force) for this experiment exceeds the permeance corresponding to the 2010 DOE target flux. This result also suggests that transition metal carbides might also be used as protective coatings for Pd and Pd alloy membranes. Lastly, the $\text{Mo}_2\text{C}/\text{V}$ composite membranes were shown to be

stable for at least 168 hours = one week, including cycling at high temperature and alternating He/H₂ exposure.

1. Introduction and Background

Project Objective

The objectives of this research project was to fabricate, characterize, and optimize high temperature, hydrogen permeable membranes based on transition metal carbides to separate hydrogen from gas mixtures at high temperatures and pressures representative of gasification of carbon feedstocks such as coal or biomass to meet DOE NETL 2015 hydrogen membrane performance targets, summarized in Table 1-1 below[1]. Synthetic parameters such as pore size, carbide formation conditions, and the thickness of the carbide layer will be varied to study the effects on the performance of the metal carbide composite membranes. As we expect that molybdenum carbide and other related compounds such as sulfides and nitrides will be very robust chemically, we also investigated the effect of gas mixtures on the performance (permeance and selectivity) of the metal carbide, composite membranes.

Background

Approximately 80% of the global energy demand comes from fossil fuels, including coal, petroleum, and natural gas, and this reliance on fossil fuels is expected to increase at least until the year 2020. Combustion of these fossil fuels to generate power produces CO₂. There is growing scientific evidence that rising CO₂ levels in the atmosphere have and will continue to produce climate change. As a result, a number of strategies are being explored to efficiently separate and store CO₂. This will be easier to accomplish from large stationary sources such as fossil fuel based power plants compared to mobile platforms, i.e., automobiles. Fossil fuel-based power plants figure prominently in the list of stationery sources from which the U. S. produces over 50% of its electricity. An MIT report concludes that the US must develop and test new technologies to capture and store CO₂ from coal-fired power plants[2]. High temperature, inorganic membrane technology is being investigated to perform many of the separations needed for co-generation of electric power or hydrogen from fossil fuels while simultaneously concentrating and capturing CO₂.

Table 1-1. DOE Fossil Energy Hydrogen Membrane Performance Targets

Performance Criteria	2010 Target	2015 Target
Flux SCFH/ft ² @ 100 psi ΔP H ₂ partial pressure, 150 psia feed and 50 psia permeate pressures or 100 psi ΔP	200	300
Operating temperature range (°C)	300 to 600 °C	250 to 500 °C
ΔP operating capability, system pressure (psi)	400	800 - 1000
Sulfur tolerance	20 ppm	>100 ppm
Hydrogen permeate purity	99.5%	>99.99%
CO tolerance	Yes	Yes
Water-gas-shift catalytic activity	Yes	Yes

CSM used a dual synthesis strategy for the metal carbide based membranes. In the first approach, we fabricated and characterized novel, high temperature, surface diffusion membranes for hydrogen separation based on metal (Mo or W) carbides and sulfides. These membranes contain no platinum group metals (PGMs) such as Ru, Rh, Pd, Os, Ir or Pt. These same materials are used commercially in a variety of catalytic reactions including the water-gas shift with and without H₂S. Prior work at CSM has shown that a porous Mo₂C layer facilitates surface diffusion of hydrogen that is thermally activated up to 600 °C. In prior work, the pure hydrogen permeance was 3.2×10^{-6} mol/m².s.Pa, consistent with the literature for both surface diffusion membranes containing PGMs and microporous membranes. In our preliminary studies, a maximum ideal H₂/N₂ separation factor of six was observed at 600 °C and was twice the Knudsen diffusion value measured for the unmodified substrate tube. The low selectivity was attributed to the defects in the Mo carbide layer exposing large 0.2 micron (200 nm) pores from the substrate tube.

The CSM synthesis strategy consisted of the use of a low temperature, plasma-enhanced, chemical vapor deposition (PECVD) process to form a dense metal oxide layer on tubular, stainless steel filtration membrane from the Pall Corporation. The dense metal oxide layer will then be converted to a carbide phase containing small nanopores (2-3 nm) via a reduction process in a hydrocarbon/hydrogen environment. Tests will be used to identify membranes with larger pores that will subsequently be repaired to eliminate non-selective transport by viscous flow. Robust, porous stainless steel substrates will be used which will facilitate high temperature sealing and can be scaled up as they have been modularized for industrial scale filtration by the Pall Corporation.

Our second synthetic approach was to use metal carbide coated/BCC metal membranes. Palladium and palladium alloys have dominated dense metal membrane research due to the fact that they are able to both self-catalyze the hydrogen dissociation reaction and rapidly permeate the dissociated hydrogen. As shown in Figure 1-1, several crystalline, BCC-structured elements (V, Nb, Ta, and V alloys), conversely, have much higher permeability for the dissociated H species than Pd, but have limited catalytic activity for the hydrogen dissociation reaction [3]. This issue is typically addressed by coating the super-permeable BCC metal with a thin catalyst layer that is active for hydrogen dissociation, such as palladium [4]. A schematic diagram of such a composite membrane structure is shown in Figure 1-2. The resulting membranes have a narrow range of operating temperatures, as too low of a temperature will promote embrittlement of the BCC metal membrane layer, while too high of a temperature will cause alloying of the catalytic layer with the permeable layer and result in loss of permeability. A low-cost hydrogen dissociation layer that can operate at higher temperatures than a metallic catalyst would therefore be both a novel discovery and potentially a great spur to development of BCC-phase dense metal membranes. In this research project, we have shown that metal carbides can be sputtered on V foil membranes and these composite structures perform very well as high temperature hydrogen membranes[5, 6].

Figure 1-1. The influence of temperature on the pure gas hydrogen permeability of selected metals. Data for V, Ta, Nb, Pd, and Fe from Steward[7]. PdAg₂₀ data from Holleck [8] and VNi₁₅ data from Nishimura [4].

Figure 1-2. Schematic of a metal-metal composite membrane for hydrogen separation consisting of a hydrogen dissociation catalyst on both sides of a Group V metal with a BCC crystal structure. Figure adapted from Mundschau[9].

The organization of this report is as follows. The experimental apparatus and methods are presented in Chapter 2. Chapter 3 is adapted from a published journal article describing our methods for fabricating Mo_2C thin films. Molybdenum carbide, surface diffusion membranes are described in Chapter 4. Chapters 5 and 6 are also adapted from published journal articles and they present data for the Mo_2C coated, BCC metal membranes. This class of membrane was the most successful in this project. The most recent data with Mo_2C coated, BCC metal membranes are given in Chapter 7. Finally, Chapter 8 presents our conclusions.

2. Experimental Methods and Equipment

2.1 Plasma-enhanced Chemical Vapor Deposition

Figure 2-1 displays a schematic diagram of the custom plasma-enhanced chemical vapor deposition reactor that was constructed during this project. This was used to produce MoO_3 thin films and coatings that were subsequently carburized to form nanoporous Mo_2C for use as permselective membranes. The reactor employs a conventional, parallel plate geometry with the showerhead serving as the powered electrode with the rest of the chamber grounded. A 13.56 MHz RF power supply coupled to an automatic match network was used to generate the plasma. The gasses were delivered through a manifold with electronic mass flow controllers (MFCs). The precursor, molybdenum fluoride (MoF_6), was diluted with argon and delivered through the showerhead to ensure uniform delivery. Oxygen and hydrogen were supplied in great excess and were delivered into the background of the chamber. The overall reaction is:

Planar substrates were affixed to the top of the reactor. To enable the reactor to coat tubular membrane supports a customized vacuum rotary feed through was purchased from Transfer Engineering and mounted onto a 2.75" Conflat flange. This allowed the tubular supports to be placed and rotated in the center of the plasma for uniform film deposition. In addition, the feed through was connected to N_2 supply and pressure which enabled the leak rate to be measured in situ without breaking vacuum.

Figure 2-1. Schematic of the custom PECVD reactor constructed in this project.

2.2 Sputter Deposition of Mo_2C

Magnetron sputtering of dense molybdenum carbide films was performed in an AJA Orion sputter chamber shown in Figure 2-2. The system contains 4 targets and both RF and DC power supplies. Mo_2C was sputtered using RF power supplies due to charging concerns. The system has a load lock which is used to introduce planar samples such as vanadium foils onto a temperature controlled susceptor which is rotated to ensure uniform deposition. To enable the coating of tubular supports, the system was modified by again mounting a rotary feed through opposite the load lock. Samples were centered above the Mo_2C as shown in Figure 2-2 and rotated during deposition to ensure uniform coating of the supports.

Figure 2-2. Photographs of the exterior (left) of the AJA sputter chamber and the interior (right) of the system which shows how tubular supports were mounted.

The sputter rate was determined using a combination of cross-section microscopy for relatively thick layers and spectroscopic ellipsometry for coatings < 50 nm. Figure 2-3 display cross section micrographs from a film that was sputtered for 90 minutes. Using the measurement software package the film was estimated to be 192 nm, or a rate of 2.1 nm/min.

Figure 2-3. Cross-section micrographs of Mo_2C films sputtered on silicon for 90 minutes.

Most of the coating used in $\text{Mo}_2\text{C}/\text{V}$ composite membranes are much less than 50 nm and difficult to image via scanning electron microscopy. We found that variable angle spectroscopic ellipsometry (VASE) was a convenient approach to measure film thickness when using a Lorentz model to account for the conductivity of the film (Mo_2C is considered a semi-metal). Figure 2-4 plots the Mo_2C as a function of sputtering time as measured by VASE and FESEM. VASE works very well for films < 50 nm, as thickness is directly proportional to sputter time. Moreover, extrapolation of this rate is in good agreement with DFESM measurements at longer sputter times. For films > 50 nm the VASE measurements deviate from the linear expectation and the quality of the fits deteriorates as reflected in the large error bars. At these thickness a substantial portion of the polarized light is absorbed in the film, which attenuates the

accuracy of the VASE technique. Nevertheless it is very useful for the < 50 nm films which are employed in the composite membranes.

Figure 2-4. Mo₂C film thickness as a function of sputter time as determined by VASE and FESEM.

3. Formation of Mo₂C Thin Films¹

Abstract

Thin films of stoichiometric β -Mo₂C were fabricated using a two step synthesis process. Dense molybdenum oxide films were first deposited by plasma-enhanced chemical vapor deposition using mixtures of MoF₆, H₂, and O₂. The dependence of operating parameters with respect to deposition rate and quality is reviewed. Oxide films 100 – 500 nm in thickness were then converted into molybdenum carbide using temperature programmed reaction using mixtures of H₂ and CH₄. X-ray diffraction confirmed that molybdenum oxide is completely transformed into the β -Mo₂C phase when heated to 700 °C in mixtures of 20% CH₄ in H₂. The films remained well-adhered to the underlying silicon substrate after carburization. X-ray photoelectron spectroscopy detected no impurities in the films, and Mo was found to exist in a single oxidation state. Microscopy revealed that the as-deposited oxide films were featureless, while the carbide films display a complex nanostructure.

Introduction

Molybdenum carbide is a versatile material with potential applications in a variety of areas. Molybdenum carbide exhibits catalytic properties analogous to platinum group metals, and in the last few decades efforts have been made to exploit this trait in a number of chemical processes including ammonia synthesis, hydrocarbon reforming, water gas shift, H₂ production, and alcohol synthesis.[10-16] As a thin film, the high hardness and thermal stability of the transition metal carbides make them useful as wear-resistant materials.[17, 18] More recent studies have focused on the optoelectronic properties of molybdenum carbide for a range of applications including mirrors,[19] diffusion barriers,[20] interconnects,[21] and electron field emission.[22] Our interest is in the creation of inexpensive alternatives to platinum group metals for surface dissociation of H₂. Formation of this material as a thin film would facilitate fundamental studies of catalyst performance.

Numerous techniques have been used to deposit molybdenum carbide films including chemical vapor deposition (CVD),[17, 23] physical vapor deposition (PVD),[18, 20] and electrodeposition.[24] The Mo-C system is quite complex, with numerous stable and metastable compounds and crystal phases that have been observed.[23, 25] Control of phase purity has been problematic for both CVD and PVD approaches, and films often contain a mixture of carbon-

¹ This chapter is a reformatted version of the following journal article: Wolden, C.A., Pickerell, A., Gawai, T., Parks, S., Hensley, J., Way, J.D., "Synthesis of β -Mo₂C Thin Films", *ACS Applied Materials & Interfaces*, **3**(2), 517-521 (2011).

rich products that display a complex dependence on the specific operating conditions employed.[17, 20, 23] In contrast, for catalysis applications it is relatively straightforward to achieve the desired β -Mo₂C phase in powder form.[10-13] The key development came from Boudart and coworkers[10, 11] who developed a method to convert dense MoO₃ powders into high surface area Mo₂C by temperature-programmed reaction or TPR, using mixtures of hydrocarbons diluted in H₂. The mechanism for the MoO₃ to Mo₂C transformation involves the substitution of carbon for oxygen in the MoO₃ lattice, with little displacement of the Mo atoms during the reaction. Because the molar volume of Mo₂C is smaller than the molar volume of MoO₃, micropores form as the oxide transforms into the carbide. Under proper conditions the MoO₃ is converted into Mo₂C without forming metallic Mo as a reaction intermediate. Metal sintering is avoided using this method, and unsupported catalysts can be prepared with very high surface areas (50 – 90 m²/g). Rebrov et al.[14] used this strategy to form catalyst coatings through the carburization of pre-oxidized molybdenum sheets, and applied them to the water gas shift reaction.

The goal of this work was to produce phase pure β -Mo₂C films for future study as model catalyst layers. Below we describe a two step synthesis approach. First, dense molybdenum oxide films are deposited on silicon using plasma-enhanced chemical vapor deposition (PECVD) using mixtures of MoF₆/H₂/O₂. The use of MoF₆ and this reaction chemistry is somewhat unique, as previous CVD of Mo-containing compounds have employed either Mo(CO)₆[26, 27] or MoCl₅[23, 28] as the molybdenum precursor. The dependence of oxide growth rate and quality on PECVD parameters is described. The use of PECVD to form the oxide allows these films to be produced on a broader set of substrates. The films were then transformed into the β -Mo₂C phase by applying TPR conditions developed by the catalysis community. The evolution of film composition and structure throughout these processes is quantified using a suite of analytical techniques.

Experimental Section

Oxide Synthesis.

Molybdenum oxide films were deposited using mixtures of MoF₆/H₂/O₂ in a capacitively-coupled PECVD system. This PECVD chemistry adopts a similar approach that has been successfully applied for the synthesis of electrochromic WO₃ films using analogous gas mixtures (WF₆/H₂/O₂).[26, 29] Molybdenum hexafluoride (Acros Organic, 99.5 vol. %) decomposes readily, however the reaction is reversible as the released fluorine radicals will etch the film. To mitigate this issue hydrogen is added to scavenge atomic fluorine, forming HF. Oxygen is also

supplied in excess to ensure fully oxidized films. All depositions described here were conducted at ambient temperature with the plasma power fixed at 200 W. MoF₆ was delivered using a calibrated needle valve, while electronic mass flow controllers were used for O₂ and H₂ flowrates. The reactor was pumped using a Fomblin-equipped mechanical pump (Edwards, E2M40) with deposition pressures in the range of 500 – 700 mTorr depending on total flowrate.

Carburization.

The carburization process was conducted by TPR in a temperature-controlled flowtube using conditions adopted from the literature.[10, 11] Initial studies employed commercial MoO₃ powders (Sigma-Aldrich, 99.5%) to verify the efficacy of the process. Approximately 1 g of powder was placed in a crucible, inserted into the flowtube, and calcined using 200 sccm of bone dry air at 500 °C for an hour to desorb any moisture. The gas was then switched to a 20 vol. % CH₄/H₂ mixture at a total flowrate of 500 sccm, and the temperature was ramped at a rate of 1°C/min up to 700 °C, where it was held for 3 hours. After carburization the furnace was turned off and samples were cooled to room temperature under the flow of industrial grade nitrogen, which also served to passivate the carbide prior to exposure to air. Oxide films were transformed into the molybdenum carbide using the identical procedure.

Characterization.

Spectroscopic ellipsometry (SE, J. A. Woollam) was used to determine the oxide film thickness and refractive index of the as-deposited films. All indices of refraction are taken at 580 nm. Measurements were taken at an angle of 70°, and data was collected over the range of 400 -1300 nm. X-ray diffraction (XRD, Siemens Kristalloflex 810) was performed using a Cu K α radiation source to determine the growth orientation of the thin films using a scan rate of 3 °/min with a step size of $2\theta = 0.05$. X-ray photoelectron spectroscopy (XPS, Kratos) was performed ex situ using an Al K α X-ray source. The base pressure of the analysis chamber was <10⁻⁹ Torr, and high resolution spectra of individual binding states were recorded using a scan time of 60 seconds at a pass voltage of 40 eV. The binding energy scale was calibrated by positioning the adventitious C 1s peak at 284.6 eV,[30] and in the figures below spectra are offset for clarity. Samples were examined both as-received and after an Ar ion sputter treatment. The sputter cleaning time was set at 2 minutes, which was found to be the minimum time required to remove adventitious carbon. Information on film morphology and surface roughness was obtained by field emission scanning electron microscopy (FESEM, JEOL JSM-7000F) and by atomic force microscopy (AFM, Digital Instruments Nanoscope III) operated in tapping mode.

Results and Discussion

Molybdenum Oxide Synthesis.

The trends observed in this work are nominally identical to those reported previously for PECVD synthesis of WO_3 from $\text{WF}_6/\text{H}_2/\text{O}_2$. [29] The deposition rate scales to first order with MoF_6 flowrate, and this value was fixed at 5 sccm for the results reported here. Important values for optimizing rate and quality are the ratios between the precursor and its co-reagents O_2 and H_2 . Figure 3-1 displays the effect of these parameters on deposition rate and refractive index. First, note that oxygen is supplied in great excess in all experiments. The rate was relatively insensitive to O_2 at ~ 40 nm/min, declining slightly as the ratio is increased (Fig. 3-1a). Refractive index measurements can be taken to be an indication of film density, and it has been shown that high values have been correlated with low hydrogen content. [31] The refractive index at 580 nm is essentially unchanged at a value of ~ 2.2 , and this value is among the highest values reported in the literature for as-deposited films. [32] This indicates that O_2 is being supplied in sufficient excess.

In contrast, the rate and quality are quite sensitive to the $\text{H}_2:\text{MoF}_6$ ratios. Note that continuous, well-adhered films could not be formed with $\text{H}_2:\text{MoF}_6$ ratios less than 3. At sub-stoichiometric ratios appreciable concentrations of atomic F are present, which is deleterious to film growth. When supplied in excess the H_2 will react with O_2 to form water or possibly be incorporated in the film as $\text{MoO}_3\cdot\text{H}$, which results in an electrochromic response. Films discussed below were deposited using ratios of $\text{O}_2:\text{MoF}_6 = 50$ and $\text{H}_2:\text{MoF}_6 = 4$.

XPS was used to further examine the composition and bonding within the as-deposited films. One concern with the use of MoF_6 as a precursor is the possibility of fluorine incorporation. Figure 3-2 displays high resolution spectra of the F1 s core region. A small amount of fluorine is detected on the surface of the as-deposited film. However it is completely removed using the Ar^+ sputter clean, and no F is detectable within the films. The film composition was further examined by looking at the Mo 3d region, which is shown in Figure 3-3. The spectra in Figure 3-3 were obtained without sputter cleaning, since molybdenum oxide is substantially reduced by this process. The Mo signal is split into the Mo 3d_{5/2} and Mo 3d_{3/2} doublet caused by spin-orbit coupling. [33] Table 3-1 summarizes the location of the Mo 3d_{5/2} signal reported in the literature for various oxidation states. [13, 17, 30, 34, 35] The observed peak position of the as-deposited film at a binding energy (BE) of 232.8 eV is in good agreement with the Mo^{+6} state of fully oxidized MoO_3 . The d orbital peaks are separated by 3.1 eV and appear in the theoretically expected 3:2 ratio, [33] providing further support that the Mo is present in a single oxidation state. Of course hydrogen cannot be detected by XPS, but the position of Mo spectra in its fully

oxidized state supports its absence. XPS analysis of molybdenum oxide films intercalated with H display the presence of Mo^{+5} and Mo^{+4} oxidation states.[30] Moreover, the transparent nature of the film provide further support for its chemical purity, since MoO_3H_x has a grey color that is exploited in electrochromic applications.[30, 36]

Figure 3-1. Graphs showing the dependence of molybdenum oxide growth rate (left axis) and refractive index (right) as a function of (a) $\text{O}_2:\text{MoF}_6$ ratio and (b) $\text{H}_2:\text{MoF}_6$ ratio.

Figure 3-2. High resolution XPS spectra of the F 1s region obtained from an as-deposited MoO_3 films and after sputter cleaning.

Figure 3-3. High resolution XPS spectra of the Mo 3d region obtained from an as-deposited MoO_3 film, and after carburization.

Table 3-1. Summary of the binding energy positions reported in the literature (± 0.2 eV) for the Mo 3d_{5/2} and C 1s core levels in oxidation states of interest to Mo₂C formation.

State	BE (eV)
Mo ⁶⁺	232.9
Mo ⁵⁺	231.8
Mo ⁴⁺	229.9
Mo ³⁺	228.8
Mo ²⁺	228.2
Mo ⁰	227.6
Carbide C	283.0
Graphitic C	284.5

Carburization.

Molybdenum oxide films with thickness of 100 - 500 nm were deposited on pieces of (100) silicon wafers as described above. These samples were then carburized using standard TPR conditions described above. Films remained well-adhered to the underlying silicon substrate after carburization, and were characterized using the techniques described below. The changes in crystal structure that were observed in conjunction with TPR are summarized in Figure 3-4, which compares results from both powder samples and a 200 nm thick film with literature standards. The stable phase of molybdenum oxide has an orthorhombic structure,[36] and the as-received powders were in good agreement with the literature standards (JCPDS 76-1003).

The as-deposited oxide films are XRD amorphous, however they crystallize when annealed in air at temperatures >150 °C. During the carburization process the oxide films are transformed during the calcining step, and an example of a XRD pattern obtained from a film after this treatment is shown in Fig. 3-4. The pattern obtained from the thin film sample is noisy relative to the powder samples, but nevertheless the film is clearly identified as polycrystalline molybdenum oxide with a preferential orientation in the (110) direction located at $2\theta = 23.33^\circ$.

The same materials were examined after the completion of the carburization process. Again it is observed that the powder samples are in perfect agreement with literature expectations for the β -Mo₂C phase. Note that the β -Mo₂C phase has an orthorhombic crystal structure (JCPDS 79-0744), though its lattice positions are nominally identical to a slightly strained hexagonal closed packed structure (JCPDS 35-0787), and it has often been described as such in the catalyst literature.[25, 37] Both carbide powders and films display the three significant peaks at 2θ of 34.4, 37.9, and 39.4 which are indexed as the (100), (002), and (101) planes of β -Mo₂C, respectively. There is no evidence of residual oxide, molybdenum metal, or any other crystalline

phases of molybdenum carbide. The XRD pattern obtained from a carburized film is nominally identical to both the literature values and the powder sample, confirming its transformation to the β -Mo₂C phase.

Figure 3-4. Comparison of XRD patterns obtained from oxide powder and a 200 nm oxide film before (bottom) and after (top) the TPR carburization process. Literature values obtained from JCPDS 76-1003 (oxide) and JCPDS 79-0744 (carbide).

XPS was used to examine the composition of the carburized films. Figure 3-3 contains the high resolution spectra of Mo 3d region. The position of the Mo peaks in the carbide was shifted significantly to lower binding energy relative to the oxide film, and the peak position at BE = 228.2 eV is in perfect agreement with literature values for Mo⁺² (Table 3-1). The compositional purity of this material is again supported by both the spacing (3.2 eV) and relative intensity of the two peaks, which suggests that the Mo is predominantly in a single oxidation state. Figure 3-5 compares high resolution spectra of the O 1s region obtained from an oxide film and after carburization. The oxide film displays a prominent peak at BE = 530.8 eV, which is in good agreement with literature values.[38] The surface of the carbide is partially oxidized during the passivation step. Although the signal is attenuated substantially relative to the oxide film, there are two weak but distinct peaks at BE = 530.4 and 532.9 eV, respectively. It is speculated that the former is due to molybdenum oxide, while the latter may arise from chemisorbed CO, which is a major impurity in the industrial grade N₂ that is used during cooling before. Note that in practice, this residual oxide would be removed by reduction prior to their use as catalysts.

Figure 3-5. High resolution XPS spectra of the O 1s region obtained from an as-deposited MoO₃ film, and after carburization.

XPS was also used to examine the nature of carbon bonding in the carburized film. In studies of molybdenum carbide, including both powder and thin film form, graphitic carbon is often found to co-exist with Mo₂C. For example, high resolution transmission electron microscopy has revealed that both carbide powders and films display nanocrystalline domains coated with thin layers of amorphous, graphitic carbon.[12, 18] In this work XPS was performed ex situ, and there is always concern about distinguishing carbon germane to the sample from contamination that is present on all samples. Figure 3-6 contains high resolution spectra from the C 1s region. The bottom spectrum is from an as-deposited molybdenum oxide film, which displays the adventitious C signal common to all samples. A sputter treatment was developed to fully remove this layer (middle scan). The top spectrum was obtained from a carbide film subjected to the identical sputter treatment. The signal is dominated by a Gaussian signal positioned at BE = 283.2 eV, the position of which is in good agreement with the literature reports of the carbide phase (Table 3-1).[13, 34, 35, 39] There is also a small shoulder at higher binding energy, suggesting the presence of a small amount of graphitic carbon in the sample.

Finally the morphology of the films was studied by FESEM and AFM. The as-deposited oxide films were smooth and featureless, as one would expect for an amorphous material. Figure 3-7 displays FESEM and AFM images taken from a carburized film. The images reveal a nanostructured surface, with individual crystal sizes on the order of 50-100 nm. The RMS roughness of the films was ~11 nm, an order magnitude greater than the as-deposited oxides. As with unsupported catalysts, the details of the nanostructure are expected to be critical to the catalytic properties of the resulting films. Likewise, it is expected that the resulting nanostructure may be modified by TPR parameters (ramp rate, % hydrocarbon, etc.),[10-13] and studies are underway to examine these effects on the thin film morphology and relate them to catalyst performance.

Figure 3-6. High resolution XPS spectra of the C 1s region obtained from an as-deposited MoO_3 film, after sputter cleaning, and a Mo_2C film after the identical sputter treatment.

Figure 3-7. FESEM image of the Mo_2C film morphology. *Inset* –AFM image of a $1 \times 1 \mu\text{m}$ area from within this region.

The evidence presented above demonstrates that the two stage process described within has the ability to produce phase pure $\beta\text{-Mo}_2\text{C}$ in a thin film form. This is a distinct advantage over previous attempts to synthesize molybdenum carbide films directly through vapor deposition processes. For example, thermal CVD at 800°C produced primarily mixtures of off-stoichiometric MoC_{1-x} phases.[23] Films deposited by PECVD films were found to be carbon–

rich, with a substantial amount of impurities present.[17] Composition control has also been problematic in efforts to form molybdenum carbide by co-sputtering.[19, 20] In these vapor-phase techniques the resulting film composition is most likely controlled by the kinetics of Mo and C incorporation. In contrast, the use of oxide film growth in conjunction with the slow TPR process favors the formation of thermodynamically stable phases.[11]

Conclusions

A two step approach was introduced for the fabrication of β -Mo₂C thin films. First, it was shown that dense molybdenum oxide films could be readily deposited using mixtures of MoF₆/H₂/O₂ at room temperature. The amorphous oxide films contained no detectable impurities and displayed high refractive indices. These films were successfully converted into β -Mo₂C using temperature programmed reaction in CH₄/H₂. The phase and compositional purity of the resulting films was confirmed by XRD and XPS. The resulting films display a nanostructured morphology, and investigations are underway to assess their performance as hydrogen dissociation catalysts.

4. Mo₂C Surface diffusion membranes

Introduction

As discussed above, one of our strategies to fabricate high temperature, surface diffusion membranes for hydrogen separation is based on the formation of Mo carbide thin films on porous substrates such as porous plates or tubes. Specifically, our synthesis strategy consists of the use of a low temperature, plasma-enhanced, chemical vapor deposition (PECVD) process to form a dense metal oxide layer on a porous substrate. The dense metal oxide layer will then be converted to a carbide phase containing small nanopores (2-3 nm) via a reduction process in a hydrocarbon/hydrogen environment. Alternately, we can use sputter deposition to synthesize a Mo₂C thin film in a single step. Prior work at CSM has shown that a porous Mo₂C layer facilitates surface diffusion of hydrogen that is thermally activated up to 600 °C. In prior work, the pure hydrogen permeance was $3.2 \times 10^{-6} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa} = 5.9 \text{ ft}^3(\text{STP})/\text{ft}^2 \cdot \text{h} \cdot \text{psi}$, consistent with the literature for both surface diffusion membranes containing PGMs and microporous membranes. In our preliminary studies, a maximum ideal H₂/N₂ separation factor of six was observed at 600 °C and was twice the Knudsen diffusion value measured for the unmodified substrate tube. The low selectivity was attributed to the defects in the Mo carbide layer exposing large 0.2 micron (200 nm) pores from the substrate tube.

PECVD deposition of Mo₂C on Porous Substrates

Film Synthesis

The deposition of MoO₃ thin films was accomplished by plasma-enhanced chemical deposition (PECVD). As shown in Tables 4-1 and 4-2 below, MoO₃ films were deposited on a variety of planar and tubular membrane substrates including porous stainless steel sheet, porous alumina tubes from Golden Technologies (currently CoorsTek) and ZrO₂ coated porous stainless tubes from the Pall Corporation. Gas mixtures containing MoF₆, H₂, and O₂ were used as the PECVD precursors. All depositions were performed at room temperature with the plasma power fixed at 200 W. In general high deposition rates (> 50 nm/min) were obtained.

To optimize the deposition conditions for molybdenum oxide (MoO₃) films, planar stainless steel disks from Mott Metallurgical were used. Initial experiments were done with Mott grade 0.1 and 0.2 material with nominal pore sizes of $\sim 5 \mu\text{m}$. In order to make the surface smoother for better oxide deposition, a glassy polymer template (ethyl cellulose in acetone) was used to coat on the disk. They are dried overnight and sand paper was used to make the surface smoother for

uniform PECVD deposition of MoO_3 . All the depositions were performed for 30 minutes with the reactant flow rates optimized using silicon wafers. Results are summarized in Table 4-1.

For samples B3 and C3 shown in Table 4-1, the N_2 leak flow rate was almost zero after oxide deposition, which implies that Mo oxide completely covers the surface and blocks the pores of the substrate. Those disks were heated in air in an oven at 300 °C for 8 hours to remove the polymer template completely.

Sample C8 was templated with ethyl cellulose and then sputter coated with Mo_2C . After sputtering, this disk had no N_2 leak flow. Permeation data for this sample will be presented below.

A second cycle of oxide deposition was done on samples B1 and C1 (disks that were deposited once and had large increase in flow rates after oxide deposition) to see the effect on the flow rate and the pore size. Surprisingly, there is not much change in the flow rates after another cycle of deposition. There are several possible explanations for this observation. One possibility is that the oxygen plasma is oxidizing the polymer template during the first PECVD cycle, creating large pores that can't be blocked during the second deposition. A second possibility is that the subsequent deposition creates additional stress, which may lead to microcracks. We will investigate the use of pulsed PECVD to engineer conformal coatings that produce leak free supports.

Mo oxide was deposited on three Pall AccuSep substrate tubes as shown in Table 4-2. It was found that three 30 minute depositions was sufficient to fully seal the Pall tubes. The exception is 1737, which was visibly scratched during one of the transfers between the PECVD chamber and the leak test apparatus. This issue is being addressed through the introduction of *in situ* leak testing as described below. Pall tubes 0840 and 01737 were carburized *in situ* and permeation tested as described below.

Mo oxide was deposited on three porous alumina substrate tubes from Golden Technologies (GTC) as shown in Table 4-3. Depositions were done for 2 hour with continuous PECVD to get the N_2 leak flux through the tube as low as possible and then in-situ carburization was done as will be described below. In order to improve performance of the membrane, carburization gases were allowed to flow both on feed and permeate sides of the membrane tube. As the characterization of curved surfaces is difficult, Si wafers were placed in the carburization reactor along with the membrane. Table 4-3 below gives the deposition conditions on various GTC tubes

Table 4-1. Flow rate of nitrogen through planar supports at 20 PSI

Substrate	Flow rate before coating (ml/min)	Flow rate after polymer template coating (ml/min)	Flow rate after single MoO ₃ deposition (ml/min)	Flow rate after 2nd MoO ₃ deposition (ml/min)
B1	1800	0.215	105	115
B3	1800	0	0.04	*
B4	1800	0	74.1	*
B5	1800	16.9	8.59	32.7
B6	1800	11	176	182
C1	1700	16.9	295	296
C3	1700	22	0	*
C4	1700	0	15.9	*
C5	1700	0	71.5	177
C7	1700	1.18	181	59.3
C8 (sputter coated with Mo ₂ C)	1700	0	0 after sputter coating	

*No deposition yet

Table 4-2: Nitrogen flow rate for Pall AccuSep tubular substrates at 20 PSI

Tube no	Flow rate before deposition (ml/min)	Bubble point (PSI)	Flow rate after single MoO ₃ deposition (ml/min)	Flow rate after three MoO ₃ depositions (ml/min)
840	3820	7	38.1	0
1737	3690	41	2320	18
1738	3820	78		used for blank permeation tests
1757	3630	58	92.5	0

Table 4-3: Nitrogen flow rate for GTC porous alumina tubular substrates at 20 PSI-

Tube	Flow rate before deposition (ml/min)	Deposition time(mins)	Power and duty cycle	Flow rate after deposition (ml/min)	Further process
GTC 1	700		Pure gas permeation		
GTC 2	467		Broken		
GTC 3	701	60	200 W, Continuous	16.9	Carburized
GTC 4	735	150	100 W, 80% pulsed	3.22	Carburized
GTC 5	1650	90	100 W, 80% pulsed	0	Carburized
GTC 6	1293		Repair technique		

In the results obtained to date the amount of material deposited on the tubes was estimated by measurements of film thickness on Si wafers mounted on the surface just above the tubes. To better understand the relationship between deposition rates on the planar samples and tubes, small slivers of silicon were attached to tubes. While the rate was expected to be somewhat higher, it turned out to be greater by a factor of 5 -10. Conditions that produced smooth, well-adhered coatings on planar Si were found to produce films that cracked due to stress when deposited at the position of the planar tube. It is suspected that this issue has contributed to the delamination observed with the zirconia coatings on the Pall substrates, and may also explain the appearance of leaks in tube that initially show none after coating.

As such we initiated an investigation to reduce deposition rates and film stress through the use of pulsed power modulation and by simply decreasing the power. Figure 4-1 shows how the oxide deposition rate is reduced by decreasing the duty cycle. Note that the rates still refer to that on planar substrates. Films that deposit at rates of 10 – 20 nm/min on the planar samples result in rates of 70 – 100 nm/min on the tubes. It was observed that reducing the power to < 100 W or by operating at 200 W in pulsed mode with duty cycles < 70% resulted in the achievement of well-adhered films at the tube.

Figure 4-1. The influence of pulsed PECVD duty cycle on the oxide growth rate (GR) and the refractive index of the oxide film.

Carburization of MoO₃ Films to Produce Mo₂C

MoO₃ coated Pall AccuSep #840 and GTC tubes #3 and 5 were carburized *in situ* in a permeation test housing. A premixed gas cylinder containing 80% H₂ with the balance CH₄ was purchased based on our previous results carburizing films and powders. In summary, the carburization conditions were:

1. Heat the membrane from room temperature to 500 °C with a ramp rate of 2 °C/min in air,
2. Hold at 500 °C for 1 hour,
3. Switch to the H₂/CH₄ mixture and heat to 700 °C with the ramp rate of 1 °C/min,
4. Maintain the tube at 700 °C for 3 hours,
5. Switch to hydrogen for 30 minutes at 700 °C
6. Cool in N₂ down to 300 °C with a ramp rate of 1 °C/min
7. Perform the permeation tests from 300 to 450 °C and then cool the membrane down to room temperature.

In studies with powder samples it was observed that the total flowrate was critical to the carburization process. Figure 4-2 displays XRD patterns obtained as a function of time at T = 700 °C with a total flowrate of 37.5 sccm. Under these conditions complete carbide formation is observed after 3 hours, but the transformation occurs through metallic Mo which is clearly observed after 2 hours. To obtain the ideal nanopore morphology it is desired to convert directly from oxide to carbide, as metallic Mo is more prone to sintering. The carburization was upgraded using larger electronic mass flow controllers. Figure 4-3 displays the dependence on flowrate. At

the higher flowrate of 400 sccm, complete conversion to the carbide phase is achieved after two hours, with no evidence of Mo formation.

Figure 4-2. XRD patterns obtained from oxide powder samples as a function of carburization time at T = 700 °C .

Figure 4-3. XRD patterns obtained from oxide powders after 2 hours at 700 °C as a function of total flowrate.

Pure Gas Permeation Measurements-Pall substrate tubes

After carburization, Pall membrane #840 was permeation tested and characterized using flow porometry and SEM/EDAX. Two permeation runs were performed, in order to run high enough feed pressures to meet the pure hydrogen flux milestone.

Figure 4-4 summarizes the first set of pure gas permeation experiments and also compares the performance of the Mo₂C membrane #840 with an unmodified Pall tube. The unmodified tube data are labeled as "ideal selectivity substrate" in the Figure. The ideal selectivities of the Mo₂C

membrane are up to 33% higher than the bare tube control and range from 3.6 to 4, increasing with increasing temperature. The selectivities of the Mo₂C membrane are higher than the unmodified substrate at all temperatures. At 450 °C, the ideal selectivity of the unmodified Pall AccuSep substrate tube is just under 3. The hydrogen permeances decrease with increasing temperature, and range from 15.4 to 14.4 ft³(STP)/ft².h.psi. For comparison, the permeance associated with the 2015 pure hydrogen flux target is 3 ft³(STP)/ft².h.psi. We were initially disappointed in these data. The hydrogen flux decreased with increasing temperature, rather than showing activated transport behavior, where the H₂ flux would have increased with increasing temperature. When the flux decreases with increasing temperature, this usually suggests that the transport mechanisms are Knudsen diffusion and viscous flow. Gas viscosity goes up with temperature, therefore, the viscous flow contribution decreases and the flux drops. Viscous flow is usually associated with transport in larger pores than the 70 nm pores present in a Pall AccuSep substrate tube. The ideal separation factors did increase slightly as the temperature increased, suggesting that some of the hydrogen flux was due to surface diffusion. This trend is encouraging. However, the viscous flow contribution was so large it likely overwhelmed the selective surface diffusion mechanism.

Figure 4-4. Effect of temperature on the fluxes and ideal H₂/N₂ separation factor of Mo₂C coated Pall tube #840. Permeation tests done at a feed pressure of 2 psig.

However, when Pall membrane #840 was cooled and removed from the test housing it was apparent that the zirconia coating covering the Pall tube had delaminated in places. This was confirmed by both pore size measurements shown in Figure 4-5. The average pore size from this measurement was about 250 nm, more than three times the pore size of a typical Pall AccuSep substrate. The EDAX spectrum shown in Figure 4-6 clearly shows the presence of Fe and Ni. Since the zirconia layer is more than 30 microns thick, and the penetration depth of the x-rays is only a few microns, the Fe and Ni from the porous stainless steel should not be visible. However, due to the delamination of the zirconia layer, the underlying porous stainless steel layer was detected.

Figure 4-5. Pore size analysis performed after permeation testing of Pall tube #840.

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Figure 4-6. EDAX spectrum of the surface of Mo₂C coated Pall membrane #840 after permeation tests showing that the stainless steel substrate (Fe, Ni) is visible in the spectrum due to delamination (loss) of sections of the zirconia coating.

Due to a miscommunication with the graduate student performing the permeation measurements, flux measurements were only obtained during the first run with tube #840 with feed pressures up to 10 psig where the H_2 flux was about 100 SCFH/ft² at 400 °C. This is shown in Figure 4-7, where the hydrogen flux of membrane #840 is compared to the 2010 flux target and the flux of an unmodified Pall AccuSep substrate tube. To meet our most recent performance milestone, our goal was to show we could easily achieve the 2010 pure H_2 flux target of 200 SCFH/ft². A second permeation test was performed with Pall membrane #840 up to a feed pressure of 20 psig where the hydrogen flux was 275 SCFH/ft² at 400 °C.

Figure 4-7. The influence of feed pressure on the flux of Mo_2C coated membrane #840 for the first and second permeation tests. The fluxes are compared to an unmodified Pall substrate and the 2010 pure hydrogen flux target.

As shown in Table 4-2 above, Pall tube #01737 was also successfully coated with MoO_3 using PECVD. Since we observed that the zirconia coating for Pall membrane #840 delaminated during the permeation test, we anticipated that a similar problem might be encountered with this membrane. All of the Pall substrate tubes in Table 4-2 came from the same manufacturing batch. In order to try to avoid zirconia delamination, carburization of this tube was done with the lower ramp rate (0.25 °C/min) from 500 °C to 700 °C. Permeation testing was done and plotted as shown in the Figure 4-8 below. The permeation characteristics of this membrane are very similar to the flux and ideal selectivity of an unmodified Pall tube. The most likely explanation is that both delamination of the zirconia layer occurred along with the lack of carburization. The H_2 permeance of membrane #01737 is essentially the same as an unmodified tube, whereas membrane #840 was over a factor of two lower at the same temperature.

Figure 4-8. Effect of temperature on the fluxes and ideal H₂/N₂ separation factor of Mo₂C coated Pall tube #01737. Permeation tests done at a feed pressure of 2 psig.

Pure Gas Permeation Measurements-GTC alumina substrate tubes

Given the delamination problems with Pall tubes, a series of experiments were performed with ~200 nm = 0.2 micron pore diameter alumina tubes from Golden Technologies. These are designated as GTC tubes. As shown in Figure 4-9, the mean pore radius is ~0.1 microns = 100 nm. Permeation experiments with an uncoated, control GTC tube were performed as a function of temperature and pressure and the hydrogen and nitrogen fluxes and H₂/N₂ separation factors are shown in Figures 4-10 and 4-11. Fluxes of both H₂ and N₂ drop strongly with increasing temperature, which is consistent with transport from viscous flow and Knudsen diffusion in parallel. The viscous flow contribution is much larger than the Knudsen diffusion and therefore controls the flux. The fluxes decrease with increasing temperature because the gas viscosity increases. The volumetric flow rate is inversely proportional to the viscosity. The ideal separation factor from Knudsen diffusion is 3.74 and the experimental values decrease from about 2.7 to 2.2 (Figure 4-11) as the temperature increases from 100 to 600 °C. The actual separation factors are less than the Knudsen value due to the contribution of non-selective viscous flow.

Figure 4-9. Pore size distribution (radius) of GTC porous alumina substrate tubes.

Figure 4-10. Flux of H₂ and N₂ for uncoated GTC tube.

Figure 4-11. Ideal separation factor from uncoated GTC substrate tube.

As shown in Table 4-3 above, several GTC substrate tubes were coated with MoO₃ and the N₂ leak rate was reduced to zero or close to zero. Membranes GTC 3 and GTC 5 were carburized in-situ using the procedure give above. During the PECVD deposition of MoO₃ on GTC 3, a Si wafer sample was also coated with MoO₃ and that sample was placed in the membrane test housing during carburization. The carburized thin film sample was then analyzed using x-ray diffraction and the XRD spectrum is shown in Figure 4-12. The peaks in Figure 4-12 are consistent with the orthorhombic crystal form of Mo₂C shown in Figures 4-2 and 4-3 above.

Figure 4-12. XRD pattern of MoO_3 film carburized with membranes.

After carburization, membrane GTC 3 was cooled to 100 °C in industrial nitrogen and permeation experiments were conducted as the membrane temperature was increased up to 600 °C. The flux and separation factor data for GTC 3 are given in Figure 4-13. Note that up to 300 °C = 573 K, the hydrogen flux is increasing with increasing temperature, evidence of an activated process. The separation factor at 300 °C is 4.5, about double the separation factor for an uncoated GTC tube. Hydrogen and nitrogen flux measurements were performed at each temperature. After the temperature was increased to 400 °C, the hydrogen flux dropped by ~20%. Note that the nitrogen flux doesn't change appreciably with increasing temperature about 400 °C.

Figure 4-13. Effect of temperature on the H₂ and N₂ fluxes and ideal separation factor of Mo₂C coated GTC substrate #GTC 3. Permeation tests done at a feed pressure of 2 psig.

A similar membrane, GTC 5 was carburized in-situ and permeation tested. The hydrogen and nitrogen flux data for this membrane are given in Figure 4-14 for both increasing and decreasing temperature cycles. Only the hydrogen flux was measured in the initial temperature cycle where the temperature was increased from 100 to 600 °C. Between the experiments at 400 and 500 °C, the membrane was kept overnight in an atmosphere of flowing nitrogen. When the hydrogen flux was measured the next day, the hydrogen flux had dropped dramatically, decreasing by about 12%. The H₂ flux was then measured at 600 °C and the measurements were repeated as the temperature decreased down to 100 °C. The nitrogen flux was also measured as the temperature decreased.

Figure 4-14. Effect of temperature on the H₂ and N₂ fluxes of Mo₂C coated GTC substrate GTC 5. Permeation tests were done at a feed pressure of 2 psig.

Our working hypothesis to explain the reason for the hydrogen flux decline after exposure to nitrogen at elevated temperatures, > 400 °C, is that exposure to the nitrogen gas leads to the oxidation of the Mo₂C surface. To reduce our gas costs, we have been using industrial grade N₂ that contains up to 1% oxygen. We had previously observed that when our Mo₂C sputtered V membranes were exposed to industrial N₂, we observed a rapid flux decline. In addition, carburization will be performed using higher flowrates as discussed above to avoid formation of metallic intermediates and improve the nanostructure. Note that we always use industrial grade hydrogen for pure hydrogen permeation tests. Small amounts of oxygen in a reducing atmosphere appear to have little effect on the hydrogen flux.

Figure 4-15 presents the H₂ flux and H₂/N₂ separation factors at a feed pressure of 20 psig up to 400 °C for membrane GTC 5. Note the hydrogen fluxes are very high, exceeding the 2015 pure H₂ flux target. The separation factors are still modest, ~4, but they are roughly twice that of the uncoated, porous alumina GTC substrate. If we can eliminate the cause of the hydrogen flux decline, and further develop techniques to repair large pores, we should be able to significantly increase the separation factor while maintaining high hydrogen fluxes.

Figure 4-15. The influence of temperature on the H₂ flux and H₂/N₂ separation factor for membrane GTC 5 at a feed pressure of 20 psig.

Pure Gas Permeation Measurements-Vycor silica tubular substrates

A 4 inch symmetric and mesoporous Vycor tube [pore size ~ 4 nm; Corning Inc] which is basically 99% silica was used as substrate for oxide deposition. Since the pore size of the Vycor tube is about ~4 nm, on a bare tube the gas permeates by Knudsen mechanism only with no viscous flow. This is shown by the literature permeation data in Figure 4-16 [40]. As expected, the experimental H₂/He separation factor, or permeance ratio is 1.38, which compares very well to the theoretical Knudsen diffusion value of 1.41. If the pores were large enough to permit transport by viscous flow, the experimental separation factors will be much less than the theoretical values. The wall thickness of the Vycor tube is 1 mm and the internal diameter is about 0.83 cm.

Oxide depositions on the Vycor tube were done by following the above-mentioned procedure for 2 cycles of 30 mins each. After oxide deposition it was carburized at 700 °C for 3 hours under 80/20 H₂/CH₄ mixture to convert the oxide to carbide.

Permeation experiments were performed on the carburized tube at 300 to 500 °C and a feed pressure of 2 psig. Figures 4-17 and 4-19 show the results from the permeation experiments. As can be seen from Figure 4-17, H₂ flux increases as temperature increases while He flux decreases with temperature. This is due to the fact that the carbide layer enhances the surface diffusion of

H₂ while He is transported by Knudsen diffusion as well as blocked, to some extent, due to the adsorbed H₂. Without the carbide layer, the ideal H₂/He separation factor is 1.38 [Figure 4-16] at 500 °C or 773 K whereas with the carbide layer, the ideal H₂/He is in the range of 1.8 [@ 300 °C] to 2.4 [@ 500 °C] which clearly indicates surface diffusion of H₂. At 500 °C, the ideal H₂/He separation factor for the Mo₂C coated membrane is 74% higher. The flux values for He are lower than what would be expected if it was just Knudsen diffusion thus confirming that He flow is somewhat restricted by the adsorbed H₂. Due to the small pore size and 1 mm wall thickness of the Vycor tubes, the flux values are lower than any other porous substrates used previously [GTC and Pall tubes] but it also eliminates any viscous flow of the gases which could mask the surface diffusion contribution. This experiment supports the hypothesis that with molybdenum carbide on porous substrates, H₂ can be effectively separated from other non-interacting gases via a surface diffusion mechanism.

These data are encouraging to demonstrate that our hypothesized transport mechanism does occur. Furthermore, the Mo₂C coating on membrane Vycor-1 was deposited unevenly. We expect that the selectivity could be improved significantly by improving the quality of the MoO₃ and Mo₂C layers on the Vycor membrane.

Figure 4-16. Ideal separation factor from uncoated mesoporous silica (Vycor glass) substrate tube from Lee and Oyama[40].

Figure 4-17. The influence of temperature on the H₂ flux and H₂/He separation factor for Mo₂C coated Vycor glass membrane Vycor-1 at a feed pressure of 2 psig.

In our original proposal for this project, CSM reported H₂/N₂ permeation data for a Mo₂C/alumina surface diffusion membrane for separating hydrogen and nitrogen at temperatures up to 600 °C and a feed pressure of 5 psig. A layer of molybdenum oxide powder was coated on a porous, symmetric, alumina (GTC-200) from CoorsTek with a pore diameter of 0.2 μm and converted to Mo₂C using the TPR approach of Boudart[10]. He permeation data were also acquired and those data are shown in Figure 4-18. Interpolating the data in Figure 4-18, the

H₂/He pure gas separation factor at 500 °C is 1.76. A very similar value for the H₂/He separation factor at 500 °C of 1.73 was observed for the Mo₂C/Vycor membrane at 5 psig (Figure 19). We recognize the flux through the Vycor substrates is quite small, about 100 times smaller than for the porous alumina membrane in Figure 4-18. The experiments on Vycor glass will allow us to improve our techniques for making the MoO₃ films and carburizing them before we repeat these optimized procedures using high flux Pall AccuSep substrates.

Figure 4-18. The influence of temperature on the H₂ flux and H₂/He separation factor for Mo₂C coated GTC membrane at a feed pressure of 5 psig.

Figure 4-19. The influence of temperature on the H₂ flux and H₂/He separation factor for Mo₂C coated Vycor glass membrane Vycor-1 at a feed pressure of 5 psig.

Improving selectivity of Mo carbide surface diffusion membranes

The key issue limiting the performance of the carbide surface diffusion membranes is the presence of cracks or pinholes which means the flux is controlled by viscous flow and it is difficult to obtain the desired selectivity. The oxide PECVD parameters have been varied extensively, with the main parameters being power and duty cycle. Using these studies we have been able to form stable, crack-free coatings on silicon. However these conditions lead to film cracking and delamination when applied to the zirconia coating that covers the Pall supports. To study the morphology of the oxide deposited films and also the effect of thickness on the film's morphology, PECVD was done at optimized gas flow rates with plasma power at 80 Watts and 80% duty cycle. A thickness series ranging from 75 nm to 1300 nm was deposited on Pall button disks (similar to Pall tubes) varying the time of deposition as shown in Figure 4-20. The thickness was measured by conducting ellipsometry on the films deposited on silicon chips at the same time. It was seen that as the PECVD was carried out for longer time, it resulted in thicker films but led to cracking of the film because of the stress induced. Unfortunately, thick films are required to ensure that the underlying pores are completely coated.

Figure 4-20. SEM images of oxide film of different thickness on Pall button disc. (1. Bare disc, 2. 75nm, 3. 250nm, 4. 500nm, 5. 1285nm)

In order to rectify this issue we will pursue two strategies. The first is to perform counterflow PECVD of silica on order to reduce the average pore size of the zirconia supports prior to molybdenum oxide deposition. With smaller pores it is expected that leak free membranes can be produced with thinner molybdenum oxide films which are thus less prone to cracking/delamination. Figure 4-21 displays a schematic of the modified PECVD system. In addition to Ar, SiCl_4 may be supplied to the interior of membrane supports. SiCl_4 is inert with molecular O_2 at ambient temperatures. In principle deposition should only occur as SiCl_4 exits the pores and is exposed to atomic oxygen generated by the plasma surrounding the membrane supports. By measuring the change in pressure during deposition one may monitor the change in permeance of the support.

Figure 4-21. Schematic of the in situ pore repair set up.

Figure 4-22 provides data from initial experiments using counterflow PECVD of silica. Silica deposition was done using a mixture of 1.5 sccm SiCl₄ and 126 sccm of Ar delivered through the membrane, and 250 sccm of O₂ supplied to the exterior of the support where the plasma was ignited. PECVD was conducted at 100 W plasma power under continuous wave conditions. Figure 10 plots the increase in pressure in the line used to supply the SiCl₄/Ar mixture as a function of deposition time. The pressure difference rises linearly and then reaches a stable maximum. The reason for the stabilization was attributed to the quality of the ultratorr seal (Fig. 4-21) that was used to attach the Pall tube. It was not a perfect fit and as the pressure built up in the line, a significant fraction of the SiCl₄/Ar was released through this seal as opposed to through the pores. Nevertheless, it was found that significant pore size reduction was achieved as shown in Figure 4-23.

Figure 4-22. Pressure increase during counterflow PECVD of silica on a Pall support.

Figure 4-23. Pore size distribution in Pall tube before and after modification using silica PECVD.

Sputtered Mo₂C on Porous Substrates

Mott stainless steel disk substrates

An Mo₂C surface diffusion membrane was also fabricated by filling the pores of a disk of Mott porous stainless steel with an ethyl cellulose template and then sputter coating the disk with Mo₂C at ambient conditions. This membrane is sample #C8 in Table 4-1 above. As shown in Table 1, membrane #C8 had no N₂ leak after the polymer template was applied and remained leak-free after it was sputtered with Mo₂C at room temperature. The polymer template was then removed by oxidation by heating the disk in air at 300 °C for 8 hours. The disk was then installed in a permeation housing and pure gas permeation was measured over a range of temperatures. A control permeation test was also done with a porous stainless steel disk without modification. Figure 4-24 summarizes the permeation data with this membrane.

The permeances for membrane C8 decrease from 24 to 19 ft³(STP)/ft².h.psi as the temperature increases from 400 to 700 °C. These values were similar to the permeances measured with tubular membrane #840. In general, the same trend of permeances decreasing with temperature is observed, indicated a high % of the flux from non-selective viscous flow. This is not surprising since the mean pore size of the Mott porous stainless steel is about 5 microns. Ideal H₂/N₂ separation factors increase with temperature to a maximum of about 5 at 700 °C. At lower temperatures, the separation factors were only slightly higher than the unmodified Mott disk. In order to prepare a more selective membrane using the sputtering approach, we will need to modify the substrate with an intermediate pore size layer using an oxide such as zirconia or alumina so that the any defects in the sputtered Mo₂C layer would not expose such large pores.

Figure 4-24. Effect of temperature on the fluxes and ideal H_2/N_2 separation factor of Mo_2C coated Mott disk #C8. The Mo_2C layer was deposited on the porous stainless steel disk by sputtering. Permeation tests done at a feed pressure of 2 psig.

Vycor silica substrates

Vycor glass disks and tubes with ~ 5 nm pores, much smaller than the Motts disks described above, were ordered and were coated with Mo_2C films sputtering. For the set of experiments described below, 14 mm diameter Vycor disks [Corning Inc.] with 0.5 mm and 1 mm thicknesses were used.

The 1 mm thick Vycor disc was sputtered with Mo_2C at 200 °C for 30 mins using Ar plasma. Figure 4-25 shows the disc after sputtering. The small “unsputtered” edges on the disk are due to the tape used to stick the disk in the sputter chamber. Figure 4-26 shows the cross section of a sputtered disk. The thickness of the Mo_2C layer after 30 min deposition is about ~ 100 nm. Thus the Mo_2C deposition rate can be estimated to about 3 nm/min.

Figure 4-27 shows the permeance of various gases as a function of the inverse square root of their respective molecular weights for a 14 mm diameter and 0.5 mm thick Vycor disk at ambient temperature. Kinetic theory predicts that the velocity of a diffusing penetrant should be proportional to the reciprocal of the square root of the molecular weight if the mean free path of the gas molecule is large compared to the pore size[41]. The feed pressure was 117.2 kPa and 151.2 kPa while the permeate was kept at atmospheric pressure. It can be seen from Figure 4-27 that all the gases follow Knudsen diffusion mechanism on a bare support with no viscous flow.

Figure 4-25. Picture of a 14 mm diameter, 1 mm thick Vycor disc sputtered with Mo_2C

Figure 4-26. Cross-section [SEM] image of the sputtered disc showing ~ 100 nm carbide layer

Figure 4-27. The influence of penetrant molecular weight on permeance for various gases for 14 mm diameter, 0.5 mm thick Vycor disc at ambient temperature ($25^\circ\text{C} = 298$ K)

Figure 4-28 shows the H_2 and N_2 permeances as a function of temperature for a 14 mm diameter and 1 mm thick Vycor disk. The permeation experiments were done at a feed pressure of 117.2 kPa = 17 psia while permeate was at atmospheric pressure (82.7 kPa = 12 psia in Golden, CO). Again from this Figure, it can be seen that both the gases follow Knudsen behavior where the permeance decreases as the temperature is increased. The measured ideal H_2/N_2 separation factor is in the range of 3.3 to 3.5, close to the theoretical Knudsen selectivity of 3.74.

Figure 4-28. Permeance versus temperature for H₂ and N₂ for 14 mm diameter, 1 mm thick Vycor disc, for a feed pressure of 117.2 kPa.

H₂ and Ar permeation experiments were then done on the 1 mm thick Mo₂C sputtered disc. The experiments were done at a feed pressure of 117.2 Pa and for a range of temperatures [373.15 to 573.15 K]. Two sets of data [#1 and #2] were obtained during the permeation experiments. The membrane was kept at 373.15K under UHP Ar for two days between the two sets of data. Figure 4-29 shows the results from the permeation experiments. As can be seen from Figure 4-29, at temperatures of 373.15 and 473.15 K, for the first set of data, the H₂ and Ar follow Knudsen mechanism while at 573.15K, the H₂ permeance jumps by almost a factor of 2.5 suggesting activated surface diffusion. We were limited to these temperatures due to the seals [epoxy in this case] which starts to melt above 300 °C. The separation factor at 573.15K was 13.75, which is almost 3 times the theoretical H₂/Ar Knudsen value of 4.4. After the first run the membrane was cooled down to 100 °C under UHP Ar and left under the same conditions for 2 days. After that, the second set of permeation experiments were done and results are shown in Figure 4-7. The permeance of both the gases increased in the second run but the separation factor didn't improve and got worse. This could be due to the leak formation in the epoxy seals since it was exposed to 300 °C for quite some time during the first run. Leak in the seal will increase the flux/permeance of the gases but the separation would not improve and would become lower than the expected value from Knudsen diffusion theory.

Figure 4-29. The influence of temperature on the H₂ and Ar permeances for the Mo₂C sputtered, 1 mm thick Vycor disk membrane. The feed pressure was 117.2 kPa.

A 6" inch Vycor tube [4.7 nm pore size, Corning Inc] was sputtered with Mo₂C at 200°C for 1 hour. Pure gas [H₂ and Ar] permeation testing was then done [at feed pressure of 5 psig] on the sputtered tube and the results are shown Figure 4-30. From the figure it can be seen that as the temperature is increased, the H₂ flux increases indicating surface diffusion/active transport for H₂ whereas Ar flux remains relatively constant following a Knudsen diffusion mechanism. The ideal Knudsen separation factor for H₂ over Ar is 4.47. For the sputtered Vycor tube @400 °C the ideal separation factor for H₂ over Ar is 5.73 which is about 28% higher the Knudsen selectivity. The carbide coated membrane began showing improvements over Knudsen at temperatures as low as 200 °C degree which is highly encouraging.

Figure 4-30. Flux and H₂/Ar separation factor for a Mo₂C sputtered Vycor tube.

Transport modeling with Dusty Gas Theory

In order to satisfy an action item from the Advanced Fuels Peer Review, we have developed a transport model based on the framework proposed by Lin and Burggraaf[42]. This model calculates the individual contributions of Knudsen flow, viscous flow, and surface diffusion to permeance. The individual contributions to permeance are expressed as:

$$\text{Knudsen:} \quad P_{Kn} = \frac{1.06}{L} \frac{R}{\tau} \frac{1}{\sqrt{R_g T M}} \quad (1)$$

$$\text{Viscous:} \quad P_V = \frac{0.125}{L} \frac{1}{\tau} \frac{R^2}{\mu R_g T} P_M \quad (2)$$

$$\text{Surface Diffusion:} \quad P_{SD} = 7.75 \times 10^{-6} \exp\left(\frac{-11.705}{R_g T}\right) \quad (3)$$

where L = membrane thickness [m], R is the pore radius [m], τ is the pore tortuosity (dimensionless, assumed = 3), R_g is the gas constant = 8.314 Pa*m³/mol*K, M is the molecular

weight, m is the gas viscosity (kg/m*s), and P_M is the mean pressure based on the feed and permeate (Pa). The surface diffusion contribution was estimated based on our experimental results. The calculated Knudsen transport was subtracted from experimental measurements of hydrogen flux from experiments on Vycor glass supports where the contribution of viscous flow is negligible. This was then fit to the Arrhenius relationship shown in equation (3).

This model was tested by through comparisons with a Mo₂C coated GTC support, which is shown in Figure 4-31. As shown in this figure, there is a remarkably good agreement between experiment and model for both the total flux and the separation factor. With this in hand we applied this model to our current AccuSep supports, investigating the impact of parameters such as pore diameter, thickness, operating pressure and temperature with the goal of defining a pathway forward to meet the desired targets in terms of flux and selectivity. Figure 4-32 plots these quantities as a function of feed pressure for an Mo₂C –coated AccuSep support whose average pore size had been reduced to $D = 40$ nm. For this geometry at an operating temperature of 700 °C we identify an operating window for P_{feed} : 70 – 120 psig which satisfies both the required high hydrogen selectivity (>100:1) and flux (>200 scfh/ft²).

Conclusions

The objective of this section of the project was to explore strategies to fabricate high temperature, hydrogen selective surface diffusion membranes based on Mo carbide, a hydrogen dissociation catalyst with properties similar to Platinum Group metals. Plasma-enhanced

chemical vapor deposition (PECVD) and physical vapor deposition (sputtering) were used to deposit Mo_2C thin films on porous substrates including porous stainless steel, zirconia-coated porous stainless steel (Pall AccuSep), porous alumina, and porous silica. We were successful in demonstrating that H_2 selective, surface diffusion membranes could be fabricated by these methods to produce membranes with very high hydrogen permeances and ideal H_2/N_2 selectivities that exceed those from Knudsen diffusion, especially in the limit of high temperature and low feed pressure. These conditions minimize the contribution of non-selective viscous flow. The performance of the best surface diffusion membranes is summarized in Table 4-4 below. Membrane C-8, a Mott porous stainless steel disk sputtered with Mo_2C , had the highest H_2/N_2 ideal selectivity of 4.9, with a very high H_2 permeance of $18.9 \text{ ft}^3/\text{ft}^2 \cdot \text{h} \cdot \text{psi}$ at 700°C and a feed pressure of 2 psig. The ideal H_2/N_2 selectivity was approximately 50% higher than an uncoated, control Mott disk.

Table 4-4. Summary of Best Performing Mo₂C Surface Diffusion Membranes

Substrate	Substrate Pore Diameter (nm)	Mo ₂ C Synthesis Method	Temperature (°C)	Pressure (psig)	H ₂ Permeance ft ³ /ft ² .h.psi	H ₂ Permeance mol/m ² .s.Pa	Gas Pair	Ideal Separation Factor
Pall #840	70	PECVD	400	2	14.4	$7.9 \cdot 10^{-6}$	H ₂ /N ₂	3.9
GTC-3	200	PECVD	300	2	6.9	$3.8 \cdot 10^{-6}$	H ₂ /N ₂	4.4
GTC-3	200	PECVD	300	20	18.4	$1.0 \cdot 10^{-5}$	H ₂ /N ₂	4.2
Mott C-8	5000	Sputter	700	2	18.9	$1.0 \cdot 10^{-5}$	H ₂ /N ₂	4.9
DOE NETL 2010 Flux Target				100	2	$1.1 \cdot 10^{-6}$		

5. Mo₂C coated V foil membranes²

Introduction

Global production of H₂ stands at 50 million tons/year, and is increasing due to continued expansion of hydrocracking operations required by low grade fuels such as tar sands[43]. Over 95% of H₂ is derived from fossil fuels such as natural gas or coal through processes such as steam reforming described by the following overall reactions:

These processes proceed through CO as an intermediate, and overall conversion is limited by the equilibrium nature of the water gas shift reaction:

This creates the need for cost-effective separation processes to purify hydrogen from these components as well as other contaminants. Hydrogen-selective membranes are of particular interest for this purpose, as they are energy-efficient and allow for co-production of hydrogen while maintaining a CO₂-rich retentate at high pressure for capture or use. Additionally, if a hydrogen-selective membrane is incorporated into a reforming or shift reactor, the removal of products can drive reactions (1-3) toward complete conversion.

A number of materials are available that selectively transport hydrogen[44-46]. Among the options, polymers are eliminated by temperature constraints, while microporous ceramic systems are limited with regard to selectivity. An appealing option is dense metal films from groups III-V of the periodic table, which transport hydrogen via a solution-diffusion mechanism. In this mechanism, hydrogen is dissociatively adsorbed onto the membrane feed surface, and dissolved into the bulk. The dissociated hydrogen is then transported by site-hopping diffusion and recombined on the low-pressure membrane permeate surface[47]. As only hydrogen can be transported in this fashion, pinhole-free films of these metals will therefore have theoretically infinite selectivity.

At present, palladium and its alloys dominate research and industrial practice in this class of materials due to their ability to both dissociate hydrogen and display high permeability across a

² This chapter is a reformatted version of the following journal article: S. K. Gade, S. J. Chmelka, S. Parks, J. D. Way, C. A. Wolden, Dense Carbide/Metal Composite Membranes for Hydrogen Separations Without Platinum Group Metals, *Advanced Materials* **23** (2011), 3585–3589.

wide range of temperatures[47]. However, widespread implementation of this technology is constrained by the exorbitant and increasing costs of Pd, shown in Figure 5-1. BCC metals such as niobium, tantalum, and vanadium and related alloys have higher theoretical hydrogen permeability than the primarily face-centered cubic palladium alloys, while costing 2-3 orders of magnitude less[3, 4, 48]. Their higher permeability is attributed to their more open lattice structure that permits greater hydrogen solubility. The factor limiting their development is that, unlike palladium, they have negligible catalytic activity for hydrogen dissociation. While research is ongoing to develop alloy materials that are able to dissociate hydrogen, the issue is more typically addressed by addition of a thin platinum group metal hydrogen dissociation catalyst layer on both sides of the bulk membrane metal [3, 49]. Palladium and palladium alloys are the most common choices for this catalyst layer. This increases the cost of the membrane and lowers hydrogen transport rates due to the lower permeability of the catalyst. More importantly, the use of these metallic catalysts limits the available operating temperatures, as high temperatures result in intermetallic diffusion between Pd and the BCC metal, gradually depressing hydrogen permeability. Another challenge with BCC metals is that they are more prone to low-temperature hydrogen embrittlement, in which hydride phases are formed causing the metal to crack. Operating temperatures above 350 °C are therefore extremely desirable to mitigate this problem[49]. These two issues combine to severely constrain the temperature window in which BCC metals may be effectively employed for H₂ separation.

Figure 5-1. Historical commodity prices for Pd.

This study assessed the potential of molybdenum carbide to serve as stable catalysts for H₂ dissociation in high temperature membrane applications. The catalytic properties of transition metal carbides, particularly those of tungsten and molybdenum, were recognized in pioneering work by Boudart's group[50]. These carbides, and analogous sulfides, have been pursued as substitutes for precious-metal catalysts in reactions requiring hydrogen oxidation/dissociation, such as in fuel cells or water-gas shift reactors[51-54]. Although they are not necessarily intrinsically hydrogen permeable, dissociated hydrogen readily diffuses along their surfaces. The hypothesis which provoked this research is that thin layers of carbides may allow for the transport of dissociated hydrogen to the underlying metal along grain boundaries or micro-scaled defects. The carbides are mechanically durable and have extremely high melting points, which should make them less prone to alloying with the base metal and enable stable operation at high temperature. The proposed carbide/metal composites contain no platinum group metals, which reduces material costs by orders of magnitude relative to Pd-based systems.

Experimental

Cold-rolled vanadium foils 50.8 micron in thickness with 99.8-99.9% purity were purchased from ESPI Metals and cut into circular samples, each 1.19 cm in diameter. As received V foils contain a layer of native oxide, which hinders hydrogen transport. This layer was removed by an Ar ion sputter treatment at a pressure of 25 millitorr and 100 watts for five minutes at room temperature, which produced a DC bias voltage of 300 ± 1 volts on the substrate. The foils were then heated to their respective sputtering temperatures under vacuum. Molybdenum hemicarbide (Mo₂C) catalyst layers were deposited directly onto the clean V surface without breaking vacuum by RF sputtering (AJA Orion) in Ar at 5 mtorr using 100 W of power. All films were deposited for 30 minutes, producing films ~65 nm in thickness. The cleaning and sputtering process was performed on both sides of the foil to facilitate dissociation upstream and recombination downstream. To facilitate characterization by XRD and AFM, carbide was deposited on silicon wafers at the same time as on vanadium foils. The silicon wafers, being smoother and having no conflicting x-ray diffracted peaks, permit characterization of the thin carbide layer without interference from the bulk metal's properties.

XRD (Siemens Kristalloflex 810) was performed using a Cu K α radiation, and films were scanned over a range of $2\theta = 15 - 65^\circ$ using a step size of 0.05° . AFM (Digital Instruments Nanoscope III) images were obtained in tapping mode. Sample preparation for transmission electron microscopy (TEM) employed the focused ion beam capabilities of a field emission scanning electron microscope (FESEM, FEI Quanta 3D FEG Dual Beam), while imaging was

conducted on a FEI Tecnai T20 TEM. Selected area diffraction studies and energy dispersive spectroscopy were performed using a Philips CM200 TEM.

Membranes were permeation tested by mounting in 1/2" Swagelok™ VCR fittings. The gaskets used were silver-plated nickel to provide a leak-free seal at the elevated temperatures studied while reducing possibility of hydrogen transport through the seals. This created an effective membrane surface area of 0.93 cm². A filter gasket with a nominal particle rejection size of 10 microns was placed on the permeate side of the membrane to prevent excessive mechanical distortion of the thin foil under high feed-side pressures while providing negligible resistance to flow. The test fixture was mounted in a furnace, and heated under the flow of UHP He at 1 °C/minute to the base test temperature of 600 °C. This prevents low-temperature hydrogen embrittlement of the vanadium bulk, while protecting against destructive oxidation. The membrane was then characterized by single-gas permeation experiments using industrial-grade hydrogen and UHP helium as described in Table 5-1. The permeate side of the membrane was maintained at atmospheric pressure, locally approximately 82 kPa, and no sweep gases were used during permeation testing. Permeate flows were measured using a soap film meter.

Table 5-1. Order and conditions of experiments

Experiment	Elapsed time (hours)	Temperature (°C)	Feed pressure (gauge, kPa)
Flux stabilization	0-40	600	138
Thermal cycling	40-48	600-700	138-690
Stability testing	48-168	600	690

Results and Discussion

To test this hypothesis, thin layers of Mo₂C were applied to both sides of 50 μm thick vanadium membranes by sputtering. All membranes tested had zero detectable flux of helium up to transmembrane pressures of ΔP = 690 kPa, which indicates that transport via pinholes is negligible in these structures. A control membrane with no Mo₂C catalyst layers also had no hydrogen flux, with the detection limit being 5.9 x 10⁻⁵ mol m⁻² s⁻¹ for both He and H₂. This demonstrates that the Mo₂C catalyst layer is solely responsible for enabling hydrogen dissociation and transport. All membranes coated with Mo₂C layers displayed detectable hydrogen transport.

The flux of H₂ through dense metal membranes generally obeys the following relationship:

$$J = -D_H K_s (P_{H_2, Feed}^n - P_{H_2, Permeate}^n) \quad (4)$$

where J is the flux of molecular hydrogen, D_H is the diffusion coefficient, K_s is the solubility constant, and P_{H_2} is the partial pressure of H_2 . The exponent n describing the pressure dependence can vary from 0.5 – 1 depending on the rate-limiting step. Conventional Pd membranes obey Sievert's law, which assumes that the rate of H_2 dissociation and recombination on the surfaces is much faster than transport through the bulk and the exponent in equation (4) is $n = 0.5$ [47]. This is the case for all but the thinnest palladium membranes, and for most BCC-metal membranes operated at temperatures above 400°C[3, 55]. Exponents greater than 0.5 are most often observed when the surface is poisoned, and the exponent will increase to $n = 1$ in the limit of the flux being completely controlled by the rate of H_2 dissociation .

The hydrogen flux of the most permeable material is shown in Figure 5- 2, which was a membrane with carbide catalyst layers deposited at 200 °C. All the carbide-coated vanadium composites showed poor correspondence to Sievert's law. Flux displayed a better linear relationship with pressure, rather than with $P^{1/2}$ and fitting the data give pressure exponents between 0.8 and 1 for all membranes, as shown in Table 5-2. This suggests that the surface catalyst layer is limiting the rate of hydrogen transport in these membranes, due to the lower activity of Mo_2C compared to materials such as Pd. Increasing the test temperature generally decreased the n -value particularly in the most active membranes, which would seem to bear out this hypothesis. We note that the mechanism for hydrogen transport is expected to be more complex in these composite membranes than conventional structures involving Pd. In addition to H_2 dissociation on the carbide and its transport through the bulk, there is the additional step of hydrogen transport through the carbide layer itself. These factors are discussed in Chapter 6 below.

Figure 5-2. Hydrogen flux vs. square root of the partial pressure gradient for a 50 μm vanadium foil sputtered with Mo_2C at 200 $^{\circ}\text{C}$. Inset: The same data, replotted as flux vs. pressure drop.

Table 5-2. Best-fit pressure exponents (n-values) for all tested membranes and test temperatures

Sputter Temperature ($^{\circ}\text{C}$)	Test Temperature ($^{\circ}\text{C}$)		
	600	650	700
Ambient	1.0	1.0	0.93
200	1.0	0.92	0.86
400	1.0	1.0	1.0
600	1.0	0.87	0.81

The structure of the carbide layers were varied by changing the sputtering conditions, and Figure 5-3 compares the temperature dependence of H_2 permeability of both Pd[56] and V[7] with four composite carbide membranes whose catalyst layers were deposited at different temperatures. Although the membranes have permeabilities significantly lower than vanadium's theoretical maximum, the membranes sputtered at 200 and 600 $^{\circ}\text{C}$ are comparable to palladium membranes, particularly at higher test temperatures. The observed trend of higher permeability with increased temperature provides additional support that the carbide layer limits hydrogen transport, as the permeability of bulk vanadium drops with temperature due to decreased

hydrogen solubility in the lattice [7, 48]. The activation energies extracted from the Figure 5-3 are summarized in the Table 5-3.

Table 5-3: Comparison of activation energies and pre-exponential factors for metallic hydrogen-transport membranes at temperatures from 600-700 °C. Values for Pd and V were extracted from refs. 16 [56] and 17 [7], respectively.

Cold-rolled Pd	13810	1.92×10^{-7}
Vanadium membranes		
CSM (T_{sputter} =Ambient)	52600	7.84×10^{-6}
CSM (T_{sputter} =200°C)	44200	7.34×10^{-6}
CSM (T_{sputter} =400°C)	65400	3.64×10^{-5}
CSM (T_{sputter} =600°C)	56800	3.26×10^{-5}
Bulk Vanadium	-24800	4.00×10^{-9}

The H₂ separation performance observed in Figure 5-3 was correlated with changes in crystal structure and surface morphology of the sputtered carbide. The properties of as-deposited Mo₂C as a function of sputtering temperature are shown in Figure 5-4. The X-ray diffraction (XRD) patterns obtained from as-deposited films as a function of sputtering temperature are compared with literature values in Fig. 5-4a. The film deposited at room temperature (RT) displays the cubic phase (JCPDS 15-0457), though the peaks are broad and low-intensity, suggesting that the material is nanocrystalline and/or substantially disordered. Films deposited at 200 °C retain the cubic structure, but the degree of crystallinity is dramatically improved as evidenced by the increased intensity and reduced width of the diffraction peaks. At 400 °C the crystalline nature is lost, while a further increase in substrate temperature to 600 °C suggests that the films begin to adopt the orthorhombic crystal structure (JCPDS 79-0744). There is also a minor reflection around $2\theta \sim 62^\circ$ whose origin is unclear, however all the peaks from this sample are quite broad and of low intensity.

Figure 5-3. Hydrogen permeability as a function of temperature for carbide-coated vanadium membranes fabricated at selected temperatures, compared with permeability data for bulk palladium[56] and vanadium[7].

The deposition temperature was also found to have a profound impact on film morphology, as shown by the atomic force microscopy (AFM) images presented in Figure 5-4b. The films displaying the cubic phase at RT and 200 °C display a nanocrystalline morphology that is quite smooth, with a root mean square (RMS) roughness of ~1 nm. The surface of the film deposited at 400 °C, which has no discernable crystal structure, is featureless and ultrasmooth. At 600 °C the appearance of the orthorhombic phase coincides with the return of a nanocrystalline morphology with significantly larger features and a RMS roughness of 10 nm. The observed evolution of microstructure with substrate temperature is consistent with Thornton's zone diagram for sputter-deposited coatings[57]. Comparison of Figs. 5-3 and 5-4 suggest that the carbide morphology plays an important role for H₂ transport in this system. The highest permeability was obtained at 200 and 600 °C, which displayed the highest degree of crystallinity and surface roughness, respectively. In contrast, the permeance was significantly lower in samples fabricated at RT and 400 °C which had little discernible crystal structure and a smooth surface. These findings support the hypothesis that grain boundaries play an important role in hydrogen transport through these layers. It is expected that the performance of these systems can be further enhanced by improving the microstructure, particularly by increasing the density of grain boundaries. Potential parameters to vary that may accomplish this include altering the bias voltage on the substrate, changing the sputtering pressure, and reducing the sputter time.

As discussed earlier, a critical issue with BCC membranes is the temperature stability of the catalyst layer. As shown in Figure 5-5, membranes were tested for over 160 hours at elevated temperature (≥ 600 °C) and showed no loss of hydrogen permeability. In fact, the hydrogen flux tends to improve slightly with time when held at high temperature, possibly due to slow reduction of trace amounts of molybdenum oxides formed by exposure to the atmosphere between fabrication and testing. By comparison, a palladium-coated vanadium membrane would be expected to lose 50% of its hydrogen permeability within 90 minutes of exposure to hydrogen at 700 °C[58]. This indicates that the carbide catalyst is not reduced to metallic molybdenum which would be expected to alloy with the bulk vanadium.

The stability of the carbide layers with V was examined directly using nanoscale characterization techniques. Figure 5-6 displays cross-section transmission electron microscopy (TEM) images from the best performing membranes with carbide layers deposited at 600 and 200 °C, respectively. The TEMs in Figs. 5-6a and b were obtained from a membrane fabricated at 600 °C after permeation testing. Note that all of these images contain a layer of Pt that was applied during TEM sample preparation using the focused ion beam. The interface between the carbide layer and vanadium remains very sharp after extensive testing at elevated temperatures. The composition and structure of these layers were further interrogated using selected area diffraction (SAD), convergent beam electron diffraction (CBED), and energy dispersive spectroscopy (EDS). The carbide layer is on the order of 65 nm thick, and appears to be quite dense. The inset at the upper right of Fig. 5-6a is the CBED image taken with the electron beam focused at the center of the carbide layer. The regular array reflects the crystallinity of this phase, and indexing of the reflections confirms that it is the orthorhombic phase of molybdenum carbide, consistent with the XRD pattern obtained from the as-deposited layer (Fig. 5-4a). There is significant roughness in this layer with individual features on the order of 10 nm, again consistent with the morphology observed by AFM in the as-deposited layers (Fig. 5-4b). The presence of grain boundaries are apparent in the high resolution image (Fig. 5-6b), supporting the hypothesis of their important role in hydrogen transport.

Figure 5-4. Images demonstrating the effect of temperature on Mo_2C film properties. a) XRD patterns of as-deposited molybdenum carbide films as a function of sputtering temperature. b) 1 x 1 mm AFM images and RMS roughness values obtained from films described in (a).

Figure 5-5. H₂ flux and temperature measured during extended testing of a membrane fabricated at T = 200 °C.

Figure 5-6. Cross-sectional TEM images from selected composite membranes. a) Image of a vanadium foil sputtered with Mo_2C at $T_s = 600^\circ\text{C}$ after being permeation tested with hydrogen for 168 hours, with insets showing selected area and convergent beam diffraction images obtained from the V and carbide layers, respectively. b) Detailed view of the boxed segment of image 6a at higher magnification. c) Membrane fabricated at 200°C before testing. d) Membrane fabricated at 200°C after testing. Note that Pt was deposited after testing as part of sample preparation using a focused ion beam.

The SAD pattern obtained from the vanadium region displays the expected cubic structure, and the extracted d-spacing confirms that it is the BCC phase. EDS was used to examine the composition at various positions in the sample. The EDS spectrum (Figure 5-7) obtained with the electron beam focused on the carbide layer showed mostly molybdenum as well as small amounts of both V and Pt, which reflects the spatial resolution of the instrument. The EDS spectrum obtained from the position of the vanadium SAD pattern displayed no molybdenum and contained only peaks associated with V, and was identical to spectra obtained from bulk vanadium taken far from the carbide interface (Fig. 5-7b,c). These nanoscale characterization techniques provide further confirmation that negligible interdiffusion occurs between these two materials under these conditions.

Figures 5-6 compares TEM images obtained from carbide membranes fabricated at 200 °C both as-deposited (Fig. 5-6c) and after extended testing under H₂ at elevated temperatures (Fig. 5-6d). The thickness of these layers were nominally identical to the 600 °C sample, confirming that the sputter deposition rate is independent of substrate temperature. The carbide layers synthesized at 200 °C are much smoother than those at 600 °C, which again is consistent with the AFM findings (Fig. 5-4b). Comparison of the two images shows that no significant changes occurred during testing, reflecting the stability of these composites. At high resolution (Fig. 5-6c) the carbide layers in these samples appear to have significant crystal structure, however it was not possible to obtain SAD images from the carbide region of either of these samples. This is attributed to the nanocrystalline morphology observed at 200 °C (Fig. 4b), which prevented the alignment of a single crystal zone axis with the electron beam. As expected, SAD images of the V regions from both of the 200 °C samples were identical to that shown in the 600 °C sample. In addition, EDS profiling of both of these samples yielded identical spectra to the results obtained from the 600 °C membrane (Fig. 5-7). In the lower magnification images one can detect a notable difference in morphology of the V layer directly adjacent to the carbide, and the material far from the interface. The interface region appears to have undergone some form of recrystallization. This is not a result of TEM sample preparation. It is hypothesized that this is the result of the Ar ion bombardment treatment used to remove the native oxide, since the morphology of this region was very similar in the 200 °C samples both before and after permeation testing.

Figure 5-7. Energy dispersive spectroscopy results obtained from the TEM sample shown in Figure 5-4a with the e^- beam focused on the following regions: (a) spectrum from the Mo_2C layer; (b) spectrum from the V layer near the carbide; (c) spectrum from bulk V far from the interface. Note that in these Figures the Cu signal derives from the sample holder. In addition the weak peak at ~ 1.8 kV labeled W is likely not tungsten, as none of the high energy

peaks associated with tungsten are present. This energy level also corresponds to Si, and being present at the same intensity in each spectrum it is attributed to background contamination in the system.

Conclusion

The maximum hydrogen flux demonstrated to date in this study is already at 29% of the U.S. Department of Energy 2015 goal, while meeting requirements with respect to selectivity[1]. As discussed above, further improvement in the structure of the catalyst is expected to increase the overall permeability of hydrogen in these systems. Through further improvements to the catalyst layer, optimization of the bulk BCC metal's transport properties, and/or reducing the overall membrane thickness, it is expected that this material system will produce highly competitive, cost-effective membranes for high temperature hydrogen separation.

6. Transport mechanism in Mo₂C coated V foil membranes³

Abstract

Composite membranes comprised of vanadium foils coated with molybdenum carbide catalyst layers were recently introduced as alternatives to palladium for high temperature separation of H₂. Experiments using D₂/H₂ mixtures unambiguously show that the mechanism involves dissociation, proton transport, and subsequent recombination. Temperature-dependent measurements of H₂ flux were performed on sets of membranes in which the thickness of both the V foil and the Mo₂C layers were varied in order to provide insight into the underlying transport mechanisms. It is shown that hydrogen transport through the carbide itself can be limiting for catalyst layers >20 nm. At temperatures <750 °C the flux is highly activated, suggesting that dissociation of H₂ on the carbide surface is the rate limiting step. At higher temperature the permeability decreases with temperature in good agreement with the theoretical predictions of the permeability of the underlying V metal. The permeability of these composite membranes significantly exceeds that of pure Pd, with values as high as 5.9×10^{-8} mol.m/m².s.Pa^{0.5} at 750 °C.

Introduction

Global production of H₂ stands at 50 million tons/year, and is increasing due to continued expansion of hydrotreating processes to remove sulfur as well as hydrocracking operations required by low grade fuels such as tar sands [43]. Over 95% of H₂ is derived from fossil fuels such as natural gas or coal through processes such as steam reforming. Reforming is typically followed by the water-gas shift reaction, an equilibrium limited process that yields a mixture of H₂, CO, CO₂, and H₂O. This creates the need for cost-effective separation processes to purify hydrogen from these components as well as other contaminants. Conventional technologies such as pressure swing adsorption or cryogenic separation are both capital and energy intensive. Membrane technologies offer substantial benefits with respect to energy consumption and operating costs. There is also increasing demand for high purity hydrogen for applications in semiconductor fabrication and proton exchange membrane (PEM) fuel cells.

Dense metal membranes have the ability to purify hydrogen with perfect selectivity. Palladium and its alloys dominate both research and commercial practice due to their unique ability to both dissociate and efficiently transport hydrogen [59, 60]. Challenges facing Pd-based membranes

³ This chapter is a reformatted version of the following journal article: C. A. Wolden, K. Adeyemo, R. H. J. Vervuurt, M. Ostwal, J. Douglas Way, Mechanistic studies of hydrogen transport through /V composite membranes, *Journal of Membrane Science* **427** (2013), 150-154.

include high material costs and the inherent challenges in making defect-free thin films. Composite Pd membranes also suffer from a small window of operation with respect to temperature. Below 300 °C phase separation and hydrogen embrittlement occurs, while thin composite Pd films can reconstruct at temperatures >450 °C, limiting durability [61]. The BCC metals (V, Ta, Nb) have much greater theoretical permeability for hydrogen than Pd [62], but are unable to dissociate H₂. This issue can be circumvented through the application of catalyst layers, with Pd being the most common choice [63]. Unfortunately Pd rapidly alloys with the underlying metal at temperatures ≥ 400 °C, leading to a loss of catalytic activity and hydrogen permeability.

Recently we introduced Mo₂C-coated vanadium composites as an example of a new class of metallic membranes for hydrogen separations [64]. These membranes displayed both high flux and perfect selectivity at elevated temperature. The catalytic properties of transition metal carbides, particularly those of molybdenum and tungsten, were recognized in the pioneering work by Boudart's group [10]. These carbides, and analogous nitride and sulfides, have been pursued as substitutes for precious-metal catalysts in reactions requiring hydrogen dissociation, such as hydroprocessing [65], methanol reforming [66] or water-gas shift reactors [67]. In our previous work it was shown that Mo₂C/V membranes were stable, with no loss of permeance or evidence of interdiffusion or alloy formation during extended operation at high temperature (≥ 600 °C) [64]. In this work we explore the mechanism and identify rate-limiting steps for hydrogen transport in these membranes.

Permeation Model

The mechanism of H₂ permeation through Pd-based membranes is quite well understood [68, 69]. Membrane performance is typically interpreted through the use of the following expression:

$$J = \frac{\pi_H}{L} (P_{H_2,F}^n - P_{H_2,P}^n) \quad (1)$$

The mechanism of transport through the carbide composite is also expected to occur through a dissociation – proton transport – recombination mechanism. Direct evidence for this is provided by analysis of the feed and permeate composition during experiments performed using D₂/H₂ mixtures [70]. The hydrogen was UHP grade, while the D₂ was quoted as >98% with residual amounts of HD being the primary impurity. In these experiments the composition of the feed or permeate was analyzed using a residual gas analyzer (Stanford Research Systems) housed in a differentially pumped chamber. Figure 6-1 compares mass spectra obtained from the feed with

that of the permeate stream that resulted from exposure to this mixture. The feed stream displays a mixture of pure H_2 and D_2 as expected, while significant isotopic scrambling is evident in the permeate stream. Absolute quantification is complicated by differences in both ionization cross sections and the relative pumping speeds of the three isotopes. Nevertheless, the prominence of the HD signal in the permeate stream clearly demonstrates that hydrogen transport proceeds through a mechanism that requires dissociation and recombination of molecular hydrogen.

Figure 6-1. Comparison of mass spectra obtained from the feed and permeate, respectively. Signals normalized and offset for clarity.

The mechanism of hydrogen transport through these carbide composites is expected to be more complex than in Pd. Figure 6-2 displays a schematic diagram of the composite membranes considered in this work. Note that this diagram is not to scale as the carbide layers (10 – 60 nm) are ~ 3 orders of magnitude thinner than the V foils (50 – 125 μm). In our analysis we assume that hydrogen transport proceeds through the following elementary steps:

1. External mass transport
2. Dissociative adsorption on the carbide surface
3. Hydrogen atom diffusion through the carbide layer
4. Hydrogen atom diffusion through the vanadium foil
5. Hydrogen atom diffusion through the carbide layer
6. Recombinative desorption from the carbide
7. External mass transport

Figure 6-2. Schematic of the composite membrane structure and the steps involved in hydrogen transport.

In principle, there will be additional steps involved with the transition of atomic hydrogen across various interfaces [69], but their contributions are expected to be minor and will be neglected in the present analysis. We assume that the contributions of mass transfer (steps 1&7) are also insignificant, since experiments were performed in pure H_2 to avoid complications due to concentration polarization effects which can arise during mixed gas testing [71]. Our previous work examined 60 nm Mo_2C /50 micron V composites, and in that case the exponent that provided the best fit to Eq. (1) was found to be $0.8 < n < 1$ [64], suggesting that H_2 dissociation (step 2) was a primary factor limiting rate. Steps 3 & 5 correspond to hydrogen transport through the carbide catalyst layers, which will be identical since the membranes considered in this work are symmetric. Previous TEM imaging revealed that the carbide layers are quite dense [64], suggesting that although thin they may impede hydrogen transport. Molybdenum carbide is not intrinsically hydrogen permeable, however atomic hydrogen may readily diffuse on its surface [65]. It is assumed that atomic hydrogen transport through this material proceeds through grain boundary assisted diffusion. Step 4 accounts for transport through the vanadium foil. In Pd-based membranes, H_2 desorption can become a significant factor during low temperature operation ($T < 350\text{ }^{\circ}C$). However, desorption is expected to be insignificant for the elevated operating temperatures examined in this work ($T \geq 600\text{ }^{\circ}C$).

The goal of this study was to provide further insight into the mechanism of hydrogen transport in these membranes and identify rate limiting steps. Under the assumptions described above there are three steps involved in H_2 transport across the composite membrane: dissociative H_2 adsorption, transport through the carbide layer, and transport through the vanadium. Caravella and coworkers [69] recently provided a critical analysis of the application of Sievert's law that included an evaluation of the individual rate-limiting steps. The flux of hydrogen may be

described using the following expressions for the three individual steps that are considered in this work:

$$\text{Dissociative Adsorption: } J = k_H \left(\frac{P_{H_2,F}}{P_{H_2,P}} - P_{H_2,P} \right) \quad (2)$$

$$\text{Carbide Transport: } J = \frac{\pi_C (P_{H_2,F}^{1/2} - P_{H_2,P}^{1/2})}{L_C} \quad (3)$$

$$\text{Vanadium Transport: } J = \frac{\pi_V (P_{H_2,F}^{1/2} - P_{H_2,P}^{1/2})}{L_V} \quad (4)$$

where k_H accounts for the kinetics of hydrogen dissociation, L_C and L_V are the thickness of the carbide and vanadium, respectively, while π_C and π_V represent the effective permeability of those layers. The relative importance of these three contributions was explored systematically by varying the thickness of the carbide catalyst layers and the V foil, as well as exploring performance over a broad temperature range.

Experimental Section

The membranes were fabricated from free standing foils of cold rolled vanadium purchased from ESPI Metals and cut out into circles approximately 2 cm in diameter. Membrane fabrication was accomplished by magnetron sputtering using an AJA Orion system. The as-received foils were introduced through a load lock and heated to 200 °C under flowing Ar at a pressure of 5 mTorr. The as-received foils are covered with native oxide, which is removed *in situ* using an argon sputter treatment. This was accomplished by applying 100 W of RF power to the susceptor for 15 minutes, which produced a plasma with a DC bias of ~450 volts. Deposition of the catalyst layer was performed without altering vacuum by applying 100 W of RF to a 2 inch diameter Mo₂C target, resulting in a ~330 V DC bias. The distance between the target and the rotating substrate was fixed at 8 cm, and these conditions resulted in a deposition rate of ~2 nm/min as assessed by TEM cross sections. After completion the sample was removed from vacuum, turned over, and the identical procedure was repeated to produce symmetric membranes.

The resulting membranes were then sealed for testing using commercial VCR fittings, leaving an exposed area of 0.93 cm². Membranes were then single gas tested at temperatures between 600 – 850 °C. To avoid potential embrittlement samples were heated to 600 °C under UHP grade He. We also confirmed that these membranes were perfectly selective, as no detectable transport of

He was observed. Membrane testing was performed using pure H₂ with transmembrane pressures varying from 138 – 690 kPa.

Results and Discussion

The resistance of the V itself was first examined by using foils that range in thickness from 50 – 125 microns. Figure 6-3 plots the H₂ flux versus inverse thickness at various temperatures. In this case each side of the membranes were coated with 60 nm of carbide, and these results were obtained at a trans-membrane pressure of $\Delta P = 690$ kPa. At first glance there appears to be a linear relation, suggesting that V permeability may be a rate-limiting step. This may be the case at the highest temperature, where H₂ dissociation would be rapid. However, the temperature dependence suggests that V is not the main resistance limiting transport. The permeability of V is controlled by solubility, and it is expected to decrease with temperature [62]. However, in all cases increasing temperature improved the flux, suggesting that other mechanisms are involved as well.

Figure 6-3. H₂ flux versus inverse thickness of the V foil at selected temperatures. Carbide thickness = 60 nm and $\Delta P = 690$ kPa.

To clarify the impact of the catalyst layer membranes were fabricated with the sputter time varying from 5 – 30 minutes ($L_c = 10$ –60 nm) using 50 micron V foils. Figure 6-4 plots the flux recorded versus the inverse of sputter time used to deposit the catalyst layers. In this case two

distinct regimes are observed. For carbide layers >20 nm the flux scales with $1/L_c$, suggesting that transport in the carbide is controlling the flux. In contrast, the flux saturates at each temperature examined for the thinner carbide layers, indicating mitigation of this transport resistance. The flux is highly activated, and an Arrhenius analysis of the data in the saturation regime yields an activation area of 57 ± 2 kJ/mol. This value is consistent with values reported both in molybdenum carbide catalyst literature [65] as well as for other metals [72]. This suggests that dissociation of H_2 is rate controlling under these conditions. We also note that transport resistance through the carbide layer also impacts the results shown in Fig. 3, since the carbide thickness in that series was $L_c = 60$ nm.

Figure 6-4. H_2 flux versus inverse sputter time at selected temperatures. Vanadium foil thickness = 50 micron and $\Delta P = 690$ kPa.

To better distinguish the contributions of V permeability and surface kinetics, the performance of membranes comprised of 50 micron V foils coated with 20 nm of carbide were explored over a wide temperature range. Resistance due to transport through the carbide layer should be negligible for these studies. Figure 6-5 plots the H_2 flux versus driving force for one of these membranes for a series of temperatures that range from 600–850 °C. The flux initially improved sharply with temperature before reaching a distinct maximum at 800 °C. Further increases in temperature resulted in an attenuation of the flux. These observations suggest that at low

temperature the rate is controlled by the rate above H_2 dissociation on the carbide. At sufficiently elevated temperature transport through the V becomes the rate limiting step.

Figure 6-5. H_2 flux versus the driving forces at selected temperatures. Vanadium foil thickness = 50 micron and carbide thickness = 20 nm.

This explanation is supported by the shape of the lines in Figure 6-5, which plots flux versus the square root of the pressure gradient. Non-linear regression was used to fit each curve using Eq. (1), and the best fit for n is reported in the legend of Figure 6-5. At $T = 600^\circ\text{C}$ a best fit exponent of $n = 0.93$ is obtained, which is consistent for membranes whose flux is limited primarily by the rate of hydrogen dissociation. As the temperature is increase the exponent decreases monotonically, approaching $n = 0.53$ at 850°C , consistent with a transition to the bulk diffusion-limited case.

The experimental permeability of the composite membranes was evaluated using Eq. (1) and assuming $n = 0.5$. The temperature dependence of permeability obtained from two of our membranes is compared with the experimental values for Pd and the theoretical values for the BCC metals (V, Ta, Nb) in Figure 6-6 [62]. Experimental values are unavailable due to the issues discussed in the introduction. Permeability is the product of diffusivity and solubility, and

the theoretical values of Steward are based on extrapolating measurements of these quantities made at lower temperatures. Here the two rate limiting regimes are clearly demarcated. At low temperature the flux increases exponentially as the rate of surface dissociation increases. After attaining a maximum at 750 °C the flux decreases with a slope that is consistent with the BCC metals. This optimum occurs at a slightly lower temperature than the membrane discussed in Figure 6-5. In Pd-based membranes, it is well-known that the thermomechanical history of an individual membrane can influence performance, and this is the reason for the small differences in optimal temperature. In addition, differences in the quality of the catalyst layer due to effects of target aging may also contribute to variations in performance among nominally identical membranes. The absolute values obtained are ~20% less than theoretical values for V. Note that these membranes represent perhaps the first experimental validation of Stewards predictions in this temperature range. The maximum value obtained experimentally is $\pi_H = 5.9 \times 10^{-8}$ mol*m/m²*s*Pa^{0.5} at T = 750 °C which is ~70% greater than pure Pd at these conditions.

Conclusions

We have investigated the mechanism of hydrogen transport through Mo₂C/V composite membranes by systematically varying the thickness of individual membrane components and measuring the resulting H₂ flux as a function of temperature and pressure. Transport through the dense carbide layers can limit hydrogen transport flux, however this factor is mitigated when the catalysts thickness is ≤ 20 nm. Using 50 micron V foils coated with 20 nm carbide layers it was found that the maximum flux was obtained at T = 775 ± 25 °C. At lower temperatures the rate is controlled by the rate of H₂ dissociation, an activated process with a barrier of 57 ± 2 kJ/mol. Above 750 °C the rate becomes controlled by transport through the bulk V foils, and the temperature dependence is in good agreement with theory. These findings suggest routes for further advancing this promising technology. At high temperature the flux can be improved by simply reducing thickness of vanadium, while improved catalysts will be required to enhance performance at lower temperatures.

Figure 6-6. Arrhenius plot comparing the hydrogen permeability of our membranes with experimental values for Pd and theoretical values for the BCC metals

7. Latest Developments for Mo₂C coated V foil membranes

Initial mixed gas permeation experiments

As shown in Figure 7-1, a series of permeation experiments were performed with a 30 minute sputtered, 50 micron Mo₂C V membrane at 650 °C with feed pressures up to 120 psig. The feed gases consisted of pure H₂, a 50% H₂/Ar binary mixture, a mixture consisting of 50% H₂, 25% CO₂, 5% CO, 20% Ar, and finally a water gas shift mixture (50% H₂, 25% CO₂, 5% CO, 20% H₂O). Since the feed pressures varied, we have reported permeance, or pressure normalized flux in Figure 9 to allow comparison of the performance of the membrane over the range of hydrogen partial pressure driving forces. In particular, the pure hydrogen permeation measurements were performed from 20 to 100 psig feed pressures. We assumed the dependence of flux on driving force to be linear. Over the first 20 hours of the experiment, the membrane was tested in pure hydrogen followed by the 50% H₂/Ar binary mixture. The hydrogen permeance over this time period was approximately constant at 0.25 SCFH/ft²/psi. The feed was then switch back to pure hydrogen to check for any degradation in the membrane. At that point the feed pressure was increased from 20 psig to 100 psig and the pure hydrogen flux increased by about 60% over its initial value. We have previously reported that the pure hydrogen flux of these membranes will often increase after being at high temperature for an extended time. After 26 hours on-stream, the membrane was exposed to a mixture of 50% H₂, 25% CO₂, 5% CO and 20% Ar to assess the performance in the presence of carbon species. These are the first two points shown as green triangles in Figure 7-1. The hydrogen permeance in the mixed gas environment is roughly 47% of the highest pure gas permeance. This drop in permeance is probably due to a combination of concentration polarization and inhibition due to the 5% CO in the feed gas. The mixed gas apparatus used has a limitation in that the lowest CO concentration attainable is 5% because of the range of the CO mass flow controller. After 16 hours in this feed mixture, the Ar was replaced by steam and the final data point was measured. The hydrogen permeance in the WGS mixture was the same value as we measured without the steam present.

The leak rate of this membrane was checked several times during the mixed gas test and the leak gas (non-hydrogen) flow rate was below the detection limit of our microliter flow meter. We conservatively estimate the leak rate was below .001 cm³/min. Comparing this to the permeate flow rate of approximately 10 cm³/min, this translates to a hydrogen permeate purity of $\geq 99.99\%$. It may be possible to use a gas chromatograph and/or FTIR detector to measure the purity of the permeate, but the low flow rate, due to the very small membrane area of $< 1 \text{ cm}^2$, prevented us from making that direct purity measurement. However, this estimated purity is much greater than the 2010 DOE hydrogen purity target of 99.5%.

The highest pure hydrogen flux of this membrane at 100 psig was 41 SCFH/ft² at 650 °C. Our best performing membrane, with a similar carbide layer thickness, had a flux of 120 SCFH/ft² at the same conditions. Therefore, it is likely that the performance in mixed gas could be improved by a factor of three. Better cell design may also be necessary to reduce dead volume and increase flow velocity that should reduce the concentration polarization effect and further increase the mixed gas flux.

Figure 7-1. Performance of Mo₂C/V membrane in pure and mixed gas environments at 650 °C. Feed pressure for H₂/Ar 50/50 binary mixture test was 100 psig. The feed composition for the WGS test was 50% H₂, 25% CO₂, 5% CO, 20% H₂O and the feed pressure was 120 psig.

Optimization of cell design using COMSOL modeling

A CFD modeling study using the computer program COMSOL® was performed in an effort to determine the potential impact of concentration polarization on the mixed gas experiments discussed above. We hypothesized that the poor mixing in the VCR permeation cell created a very thick concentration boundary layer in the cell that drastically reduced the hydrogen flux from the Mo₂C/V membrane during the mixed gas permeation experiment. The presence of a concentration boundary layer would reduce the flux by increasing the diffusional path length. A schematic diagram of the interior of the VCR permeation cell is presented in Figure 7-2. Our goal was to determine how the fluid dynamics inside the permeation cell affected the velocity

and concentration profiles inside the cell. Stated more simply, how does varying L , the distance from the exit of the feed gas tube to the membrane surface affect mixing in the permeation cell?

Figure 7-2. A 2-D diagram of inside of VCR fitting permeation cell showing the inner feed tube and dimensions

Figure 7-3. Calculated velocity and concentration profiles for the VCR fitting permeation cell when $L = 2.4$ inches. L is the distance from the feed gas entrance to the membrane surface. Note that the bottom $\frac{1}{4}$ of the cell has essentially no velocity resulting in a very thick concentration boundary layer at the membrane surface.

Our simulation results for two different values of L are shown in Figures 7-3 and 7-4. In Figure 7-3, the feed gas exits at about the midpoint of the cell height where $L = 2.4$ inches. This case represents our simulation of the mixed gas experiments described above. Please note that the gas at the membrane surface was essentially stagnant and the velocity was zero. This means that mass transport occurs solely by diffusion corresponding to the case where the Peclet number ($Pe = Lv/D$) approaches zero. The concentration profiles show a rather thick region above the membrane surface where the non-hydrogen gases have formed a concentration boundary layer.

Keeping all other model parameters constant, the value of L was reduced to approximately 0.5 inches. The simulation was repeated, and the velocity and concentration profiles are very different from those shown in Figure 7-4. In this case, there are a few “dead” spots in the corners of the membrane cell where the gas velocity is zero, but for most of the membrane area, we have a significant radial velocity. Furthermore, the increased gas flow has dramatically reduced the thickness of the concentration boundary layer. Note that the red color in the figure on the right hand side of Figure 7-4 represents hydrogen.

Figure 7-4. Calculated velocity and concentration profiles for the VCR fitting permeation cell when $L = 0.48$ inches. L is the distance from the feed gas entrance to the membrane surface.

Therefore, the COMSOL® simulations support our claim that concentration polarization was a probable cause of the low fluxes we observed in our mixed gas experiment with the Mo₂C coated V foil membrane. Data will be presented below for a mixed gas experiment with a Mo₂C coated V foil membrane in the future with the feed gas tube placed closer to the membrane surface.

Modifications to the pure-gas testing system were completed to facilitate mixed-gas testing with our current furnace, which can be seen in Figure 7-5. Plumbing was added to both sides of the Swagelok VCR test cell to allow the tee fitting to be outside of the After a few failed testing attempts, we applied a nickel anti-seize to the VCR fittings holding the membrane. This allowed us to open the fittings after testing and to find out that oxidation was occurring on the permeate side of the membrane.

Figure 7-5. The mixed-gas test set-up, which moved the tee-connections outside the oven. This allowed the oven to close correctly. Note the feed flow configuration is the same as in the pure-gas system – an 1/8 inch tube is inside the 1/4 inch tube and feeds hydrogen close to the membrane surface.

High permeability pure gas data

With the new feed flow configuration, an unsupported membrane (Mo_2C -3, 5 minute Mo_2C sputter on a 50 micron V foil) was mounted and tested. This is the first membrane we have tested without the frit support. This membrane had the highest flux of the Mo_2C -V system we've tested. The fluxes at 873 K are plotted in Figure 7-6. It should be noted that at 100 psi hydrogen feed pressure ($592 \text{ Pa}^{0.5}$ driving force), the DOE 2010 flux target of 200 SCFH/ft² has been reached. The hypotheses for this high flux are that the improved permeation cell configuration aided in having no boundary layer, the clean sputter chamber had no contamination in the Mo_2C layer, the thin Mo_2C layer (5 minute sputter) had minimal resistance to hydrogen permeation, and/or any transport resistance from the frit support was eliminated.

Figure 7-6. Hydrogen flux at 873 K of an unsupported membrane (Mo₂C-3) made by a 5 min Mo₂C sputter time on a 50 micron V foil.

An additional Mo₂C/V membrane was fabricated by sputtering a 50 micron vanadium foil with Mo₂C for 10 minutes. This membrane was mounted in the test cell with the feed line as close as possible to the membrane surface as discussed above. The hydrogen permeation results at $T = 600^\circ\text{C}$ can be seen in Figure 7-7 and are compared to the data from Figure 7-6. Although the membranes have similar fluxes at low driving forces, the 10 minute sputtered membrane exhibits the highest hydrogen flux of 238 SCFH/ft² ever measured at a feed pressure of 100 psig. This flux exceeds the DOE NETL 2010 pure hydrogen flux target of 200 SCFH/ft². Possible reasons for the improvement in the flux include: a clean sputter chamber or a more continuous coating of Mo₂C from the slightly longer deposition time.

In order to compare this latest membrane (Mo₂C-4) to similar membranes with high flux, we have calculated hydrogen permeabilities from the pure gas data reported in prior reports. These data are shown in Figure 7-8. We have compared the pure hydrogen permeabilities of the best performing four Mo₂C/V membranes as a function of temperature. We can also compare our data to model predictions for the permeabilities for the BCC metals (Nb, V, and Ta)[73]. Our

latest data (Mo₂C/V-3 and 4) show much higher permeabilities at lower temperatures compared to the other two top performing membranes. If you compare the latest data point at 600 °C with the three highest temperature points for membrane 2, the trend is similar to the literature predictions for Ta and V. The pure hydrogen permeability for membrane Mo₂C-4 is the highest we've ever measured at 600 °C and it is 2.8 times the permeability of pure Pd. If the hydrogen permeability is controlled by a solution-diffusion mechanism in the 50 micron V foil, then the permeability should decrease as temperature increases. This occurs because of the extremely high solubility of hydrogen in the BCC metals. The reasons for the performance increase are not known at this point, factors that would contribute to higher permeability include better cell design to decrease concentration polarization effects and less contamination in the catalyst layer due to the recently cleaned sputter chamber. Regardless, this represents a significant improvement in our baseline Mo₂C/V performance.

Figure 7-7. Hydrogen flux versus driving force of a 5 minute sputtered Mo₂C/V membrane (Mo₂C-3) fabricated compared to a 10 minute sputter Mo₂C/V (Mo₂C-4).

Figure 7-8. The effect of temperature on the pure hydrogen permeability for four 50 micron V foil membranes with Mo₂C catalyst layers on both sides. Mo₂C/V-4 sputter time was 10 minutes. Data for V, Ta, Nb, from Steward [7].

Mixed gas transport data

Mo₂C coated Pd alloy membranes

An 8.7 micron thick, tubular, PdAu10 (weight %) alloy membrane on a Pall AccuSep® substrate (CSM #407) was sputtered with Mo₂C for one hour at 200 °C. The Mo₂C layer is estimated to be approximately 60 nm thick. We performed pure hydrogen permeation tests with this membrane over a range of feed pressures up to 100 psig and temperatures ranging from 400 to 600 °C. The pure hydrogen fluxes are shown in Figure 7-9 below. At 100 psig feed pressure, the fluxes are quite high, exceeding 300 SCFH/ft² at 600 °C. From our considerable experience fabricating Pd alloy composite membranes on tubular substrates, we can estimate the pure hydrogen flux that would be expected for an 8.7 micron thick PdAu10 film on a Pall AccuSep® filter[74]⁴. As shown in Figure 7-10, the H₂ fluxes of our membrane with the Mo₂C layer are considerably less than the fluxes we would expect without the Mo₂C top layer, approximately 60% at 400 °C. This suggests that the Mo₂C layer creates significant transport resistance. We have previously shown

⁴ See Figure 3 in the cited paper from Separation and Purification Technology for a plot of pure hydrogen flux versus Pd film thickness. For the 10% Au alloy the hydrogen permeance is almost the same as pure Pd.

that the hydrogen permeability of Mo₂C coated V membranes approaches Pd at 600 °C. This is consistent with our calculations in Figure 7-10, where we estimate that the measured H₂ flux at 600 °C for membrane #407 is over 90% of that expected without the Mo₂C coating.

Figure 7-9. The effect of feed gas pressure and temperature on the pure hydrogen flux of a Mo₂C coated PdAu membrane (CSM #407)

Figure 7-10. Ratio of the measured pure hydrogen flux of the Mo₂C coated PdAu membrane to the expected flux without the Mo₂C coating at 100 psig feed pressure.

The apparent activation energy for hydrogen permeation is another important transport parameter for dense, high temperature hydrogen transport membranes. An Arrhenius plot of the logarithm of the pure hydrogen permeance (flux/ ΔP) as a function of reciprocal temperature can be created using the data in Figure 7-9. The activation energy for hydrogen permeation for the Mo₂C coated membrane is 21.1 kJ/mol, more than **twice** the value of 10.6 kJ/mol we reported for the PdAu alloy with 10 mass % Au[75]. This is further evidence that the Mo₂C layer is the controlling transport resistance in the composite structure of membrane #407.

After pure gas testing, the Mo₂C coated Pd alloy membrane was installed in our mixed gas test apparatus and a series of permeation tests were performed at a temperature of 500 °C with a total feed pressure of 100 psig. The initial tests were performed with a 50:50 binary mixture of hydrogen and nitrogen and a feed gas flow rate of 2 standard liters/minute. We then added steam to the feed mixture, a condition we refer to as the “no C” experiments. For the no C condition, the feed gas is composed of 50% H₂, 19% H₂O, and 31% N₂. After stabilization in no C, CO₂ and CO were added to the feed mixture so that the composition is the DOE 1 test condition (50% H₂, 19% H₂O, 30% CO₂, 1% CO) described by DOE NETL [1]. In each of the three cases, the hydrogen feed partial pressure and feed gas flow rate were kept constant. The hydrogen

permeate purity during the DOE 1 experiments was measured using a continuous FTIR analyzer that is sensitive for CO₂, CH₄, and CO to ppm levels.

The mixed gas permeation data for membrane #407 are shown in Figure 7-11. In order to compare these experiments to those from Figure 7-1, we are plotting hydrogen permeance instead of flux. For all three feed gas conditions the hydrogen permeances ranged from over 2 to almost 3 SCFH/ft².psi. These values are over ten times higher than those reported previously which ranged from 0.2 -0.3 SCFH/ft².psi. This difference is likely due to cell design and improved gas transport on the feed side of our tubular membrane module. As expected, the highest H₂ permeance was observed for the 50:50 H₂/N₂ feed mixture, followed by the no C condition, and the lowest flux was for the water-gas shift product mixture. The decrease in hydrogen permeance is expected since carbon monoxide and steam will occupy hydrogen dissociation sites within the Mo₂C catalyst layer. The same “competitive adsorption” phenomenon is observed with Pd and Pd alloy membranes. In addition, since Mo₂C is a water-gas shift catalyst, CO₂ and steam may be reacting to produce even more CO at the membrane surface via the reverse water gas shift reaction which would have caused “inhibition” or reduction of the hydrogen flux/permeance.

Figure 7-11. Mixed gas permeation data for Mo₂C coated Pd alloy membrane #407 at 500 °C with a feed gas pressure of 100 psig. The no C condition is the addition of steam to a binary H₂/N₂ equimolar feed gas stream.

After 30 hours on-stream, we returned to the 50:50 H₂/N₂ feed mixture and the permeance was the same as measured initially, indicating no degradation to the Mo₂C layer. The hydrogen permeance during the DOE 1 feed gas condition was relatively constant during the test also.

The hydrogen permeate purity ranged from 99.8 to 99.9% during the mixed gas permeation test. The purity declined slightly, but this was expected due to defects that probably formed in the underlying PdAu film from the pure gas testing at 600 °C. The rearrangement of the Pd film in a composite membrane at temperatures above 450 °C has been previously reported in the literature[76].

Comparing the pure and mixed gas permeation data for Mo₂C membrane #407 to the DOE NETL membrane performance targets shown in Table 1-1, we see that the pure hydrogen flux data meet the 2015 target value of 300 SCFH/ft² at 600 °C (Figure 7-9). The mixed gas hydrogen permeances also meet the 2010 Targets as they exceed 2 SCFH/ft².psi. The hydrogen permeate purity shown in Figure 7-11 was always above 99.8%, meeting the 2010 Target.

Mo₂C coated V membranes

A 50 μm V foil sample was sputtered with Mo₂C for 30 minutes on each side to fabricate two membranes for different testing conditions. A 30 minute sputter time is estimated to deposit 60 nm of Mo₂C [6]. The membranes are referred to as 10-30-12B and C. Membranes 10-30-12B and 10-30-12C were exposed to mixed-gases at 650 °C (923 K) and 150 psig (1023 kPa) feed pressure. The feed gases were mixed and pre-heated prior to being fed to the membrane cell. A temperature of 650 °C was chosen to ensure the heat loss due to high feed gas flow rates and poor oven insulation would not cause membrane embrittlement, which has been observed with V at temperatures as 575 °C. The gas mixture compositions are summarized in Table 7-1. All of the gases are industrial grade (99.0%).

Table 7-1. Gas mixtures fed to Mo₂C coated V foil membranes at 650 °C (923 K) and 150 psig (1023 kPa) feed pressure. DOE 1 is a gas mixture based on the expected composition of coal-derived syngas after a low temperature WGS reactor[1]. All mixtures were fed at a rate of 2 SLPM as that is lowest setting for accurate CO flow rates in our mixed gas measurement system.

Gases	50-50	DOE 1 [1]	CO Inhibition	CO ₂ Inhibition	Steam Inhibition
H ₂	50%	50%	99%	70%	81%
N ₂	50%	-	-	-	-
CO ₂	-	30%	-	30%	-
H ₂ O	-	19%	-	-	19%
CO	-	1%	1%	-	-

Sample 10-30-12B was the first membrane tested in mixed gas. It was stabilized with a pure hydrogen feed gas and UHP helium sweep gas before introducing gas mixtures of 50-50 H₂-N₂ and subsequently DOE 1. The resulting hydrogen permeance values during testing can be seen

in Figure 7-12. 10-30-12B was inhibited in the 50-50 hydrogen-nitrogen gas mixture and severely inhibited by the water-gas-shift gas mixture, DOE 1. The flux reduction, or inhibition in a H_2-N_2 mixture may be explained by the catalytic activity of Mo_2C for ammonia (NH_3) synthesis [78]. After 30 minutes in DOE 1, the membrane was switched back to pure-gas testing, but the pure hydrogen permeance only reached ~47% of what it was before mixed-gas testing within an eight hour recovery period.

Figure 7-12. The influence of time and gas mixture on the hydrogen permeance of membrane 10-30-12B at 650 °C (923 K) and a feed pressure of 150 psig (1023 kPa).

The second identical sample, membrane 10-30-12C, was tested in a way to understand which gas(es) caused the inhibition observed in Figure 7-12 by isolating the individual components in the DOE 1 gas mixture. The first binary gas mixture examined was 1% CO with a balance of hydrogen. This small addition of CO for 4 hours caused the hydrogen permeance to decrease as seen in Figure 7-13. When switched back to hydrogen feed the hydrogen permeance did not recover within a 12 hour period. The reason for this is currently unknown as it was unexpected that the small amount of CO would have such a drastic effect.

Figure 7-13. The influence of time and gas mixture on the hydrogen permeance of membrane 10-30-12C at 650 °C (923 K) and a feed pressure of 150 psig (1023 kPa).

Examination of Pt Co-catalysts

Our previous investigation of the transport mechanism in V/Mo₂C membranes suggested that the dissociation of H₂ on the feed side was the rate limiting step, particularly at low temperature. A recent DFT analysis of our membranes [77] identified H₂ desorption on the permeate side as a potential bottleneck. In both cases improved catalytic activity at the membrane surface would be required to improve performance. It is well known that Pt is the most effective H₂ dissociation/recombination catalysis. Moreover, it has recently been shown that monolayers of Pt deposited on Mo₂C supports creates a synergistic effect that extends catalytic activity for water-gas shift to lower temperature. To test this hypothesis we developed the capability to deposit monolayer quantities of Pt through thermal evaporation.

Pt deposition was conducted in a bell jar evacuated by a diffusion pump to a base pressure of $\sim 10^{-7}$ torr. The deposition rate was controlled by adjusting the electrical power supplied to a tungsten evaporation boat, and a shutter was used to control the thickness. The thickness was measured *in situ* using a quartz crustal microbalance (QCM). The catalytic properties of the

resulting surfaces were tested electrochemically for the onset of the hydrogen evolution reactions (HER). This electrochemical test is a quick and convenient surrogate for evaluating catalytic activity. We examined the overpotential required to dissociate H_2 from various substrates. Figure 7-14 plots data from linear sweep voltammetry (LSV) for several substrates and surfaces. In this

Figure 7-14. Current density vs. applied potential for a number of electrodes including Pt, V, and Mo_2C coated V.

LSV experiment the current density, a measure of the H_2 evolution rate, is plotted versus the applied potential. The curve on the far right was obtained from a Pt foil, which requires essentially no overpotential. In contrast an uncoated V foil, the curve to the far left, requires the greatest overpotential. We see that the sputtered Mo_2C requires a lower overpotential than either V or Mo, however it remains substantially inferior to bulk Pt. The remaining curves show the results obtained from Mo_2C -coated V with varying amounts Pt evaporated onto the surface. The addition of a few Angstroms of Pt significantly shift the onset potential, and films with 12 – 20 Å display behavior approaching pure Pt.

The onset potential is extracted by extrapolating the linear portion of the LSV to the x intercept. These data are summarized in Figure 7-15 which plots the HER potential for Mo_2C -coated V foils as a function of the amount of Pt deposited. Note that at present the QCM has not been calibrated for Pt, so the absolute values may be off by $\pm 20\%$. For reference the HER potentials

of bulk V, Mo₂C, and Pt are indicated by the horizontal lines. We see that at 4 Å the behavior remains substantially unchanged from Mo₂C, but then the behavior changes rapidly and films with > 15 Å of Pt have HER onsets nominally identical to bulk Pt. The performance of these modified membranes for high temperature H₂ separation are discussed below.

Figure 7-15. Onset potential for hydrogen evolution for bulk Pt, V, and Mo₂C (horizontal lines), compared with V/Mo₂C foils coated with varying amounts of Pt.

During the fabrication of membrane Mo₂C-4 described above, several V foil disks were sputtered with Mo₂C catalyst layers at the same time, and under the same conditions. As described above, we evaporated a very small (2 nm) amount of Pt co-catalyst on both sides of these membranes. The purpose of these studies was to try to investigate the importance of the hydrogen dissociation rate on the overall transport rate of hydrogen through a Mo₂C/V foil membrane. We also were interested in if the presence of an additional hydrogen dissociation catalyst on the permeate side could decrease the desorption resistance recently [77] postulated by Sholl.

Figure 7-16 below compares the pure hydrogen flux of membrane Mo₂C-4 with an identical membrane sputtered with 2 nm of a Pt co-catalyst on both sides at 600 °C. As we hypothesized, the presence of a very active Pt co-catalyst for hydrogen dissociation increased the hydrogen flux at both lower driving forces and lower temperature compared to the Mo₂C-V membrane. At a low driving force of $\Delta P = 20$ psi (Fig. 7-16a) the Pt-coated membrane displayed significantly greater flux than Mo₂C-4 across the full temperature range examined. Moreover, the Pt-coated membrane remained intact at temperatures as low as $T = 450$ °C, delivering substantial H₂ flow. In contrast the baseline Mo₂C-4 failed at 450 °C, presumably due to H₂ embrittlement. Similar results were obtained at $\Delta P = 100$ psi (Fig. 7-16b). At 600 °C the performance of the baseline membrane and the Pt-coated were nominally identical, however the addition of the co-catalyst substantially boosted performance at low temperature and extended it to 500 °C without embrittlement. The flux of the baseline membrane plunged when the temperature was reduced to 550 °C, and the membrane failed due to embrittlement at lower temperature. Though preliminary these results are very encouraging in that they confirm our hypothesis that catalysis is the rate limiting step at low temperature, and this issue may be overcome. In addition, it suggests that the electrochemical testing may prove to be a viable route for screening the efficacy of potential co-catalysts.

Figure 7-16. Plots of pure H₂ flux comparing a baseline Mo₂C/V membrane with a Pt-coated membrane (21 Å) as a function of temperature at (a) $\Delta P = 20$ psi and (b) $\Delta P = 100$ psi.

Conclusions

Improvements to the permeation cell design led to increases in the pure gas flux of the planar Mo₂C/V composite membranes. We have fabricated a 50 μ m thick, Mo₂C/V foil membrane that in pure gas testing delivered a H₂ flux of **238 SCFH/ft² at 600 °C and 100 psig**, with no detectable He permeance. This exceeds the 2010 DOE Target flux of 200 SCFH/ft². This flux is

2.8 times that of pure Pd at the same membrane thickness and test temperature and over 79% of the 2015 flux target of 300 SCFH/ft².

In mixed gas testing with Mo₂C coated V foil membranes, we achieved a permeate purity of $\geq 99.99\%$, satisfying the permeate purity milestone, but the hydrogen permeance was low, ~ 0.2 SCFH/ft².psi. In these initial tests, we hypothesized that the flux was limited either by concentration polarization in the membrane test cell and/or competitive adsorption from gas mixture components including steam or carbon monoxide. Further mixed gas permeation testing with a Mo₂C coated, Pd alloy, tubular membrane with the DOE 1 feed gas mixture yielded a hydrogen permeance of >2 SCFH/ft².psi which was stable during the entire test. The permeance (flux/driving force) for this experiment exceeds the permeance corresponding to the 2010 DOE target flux. This result also suggests that transition metal carbides might also be used as protective coatings for Pd and Pd alloy membranes.

Electrochemical screening by studying the hydrogen evolution reaction (HER), may be useful to evaluate other hydrogen dissociation catalysts and potential co-catalysts. These experiments allowed us to determine that a small amount of Pt on Mo₂C was essentially equivalent to pure Pt in terms of the HER performance.

Based on the electrochemical measurements, we determined that a very small amount of Pt co-catalyst, ~ 2 nm thick, significantly improved the performance of Mo₂C/V composite membranes for hydrogen transport. As we hypothesized, the presence of a very active Pt co-catalyst for hydrogen dissociation increased the hydrogen flux at both lower driving forces and lower temperature compared to the Mo₂C-V membrane.

8. Conclusions

Colorado School of Mines (CSM) developed high temperature, hydrogen permeable membranes that contain no platinum group metals with the goal of separating hydrogen from gas mixtures representative of gasification of carbon feedstocks such as coal or biomass in order to meet DOE NETL 2015 hydrogen membrane performance targets. We employed a dual synthesis strategy centered on transition metal carbides. In the first approach novel, high temperature, surface diffusion membranes based on nanoporous Mo_2C were fabricated on porous, planar and tubular substrates. These were produced in a two-step process that consisted of molybdenum oxide deposition followed by thermal carburization. Our best Mo_2C surface diffusion membrane achieved a pure hydrogen flux of 367 SCFH/ft² at a feed pressure of only 20 psig. The highest H_2/N_2 selectivity obtained with this approach was 4.9. A transport model using “dusty gas” theory was derived to describe the hydrogen transport in the Mo_2C coated, surface diffusion membranes.

The second class of membranes developed were dense metal foils of BCC metals such as vanadium coated with thin (< 60 nm) Mo_2C catalyst layers to dissociate the molecular hydrogen. We have fabricated a $\text{Mo}_2\text{C}/\text{V}$ composite membrane that in pure gas testing delivered a H_2 flux of **238 SCFH/ft² at 600 °C and 100 psig**, with no detectable He permeance. This exceeds the 2010 DOE Target flux of 200 SCFH/ft². This flux is 2.8 times that of pure Pd at the same membrane thickness and test temperature and over 79% of the 2015 flux target of 300 SCFH/ft².

The Colorado School of Mines was awarded U. S. patent #8,623,121 B2 entitled, “Stable Catalyst Layers for Hydrogen Permeable Composite Membranes,” covering these novel membrane synthesis methods. This patent can be found in Appendix A of this report.

In mixed gas testing with Mo_2C coated V foil membranes, we achieved a permeate purity of $\geq 99.99\%$, satisfying the permeate purity milestone, but the hydrogen permeance was low, ~ 0.2 SCFH/ft².psi. In these initial tests, we hypothesized that the flux was limited either by concentration polarization in the membrane test cell and/or competitive adsorption from gas mixture components including steam or carbon monoxide. Further mixed gas permeation testing with a Mo_2C coated, Pd alloy, tubular membrane with the DOE 1 feed gas mixture yielded a hydrogen permeance of > 2 SCFH/ft².psi which was stable during the entire test. The hydrogen permeate purity was $> 99.8\%$ for all mixed gas test conditions. The permeance (flux/driving force) for this experiment exceeds the permeance corresponding to the 2010 DOE target flux. This result also suggests that transition metal carbides might also be used as protective coatings for Pd and Pd alloy membranes. Lastly, the $\text{Mo}_2\text{C}/\text{V}$ composite membranes were shown to be

stable for at least 168 hours = one week, including cycling at high temperature and alternating He/H₂ exposure.

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Appendix A U. S. Patent 8,623,121 B2

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(12) **United States Patent**
Way et al.

(10) **Patent No.:** **US 8,623,121 B2**
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(54) **STABLE CATALYST LAYERS FOR
HYDROGEN PERMEABLE COMPOSITE
MEMBRANES**

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C23C 16/50 (2006.01)

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USPC **95/55**; 95/45; 95/56; 96/4; 96/11;
422/211; 427/569; 427/585; 204/192.1

(58) **Field of Classification Search**

USPC 96/4, 11; 95/45, 55, 56; 422/211;
427/243, 532, 569, 585; 204/192.1

See application file for complete search history.

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ABSTRACT

The present invention provides a hydrogen separation mem-
brane based on nanoporous, composite metal carbide or metal
sulfide coated membranes capable of high flux and permse-
lectivity for hydrogen without platinum group metals. The
present invention is capable of being operated over a broad
temperature range, including at elevated temperatures, while
maintaining hydrogen selectivity.

28 Claims, 12 Drawing Sheets

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10 (a)

Figure 10 (b)

Figure 10 (c)

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STABLE CATALYST LAYERS FOR HYDROGEN PERMEABLE COMPOSITE MEMBRANES

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority under 35 U.S.C. §119(e) to U.S. Provisional Patent Application Ser. No. 61/316,142 filed Mar. 22, 2010, which is incorporated herein in its entirety by reference.

STATEMENT OF GOVERNMENT INTEREST

This invention was made with government support under grant number DE-FE0001009 awarded by the Department of Energy through NETL. The Government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention provides a hydrogen separation membrane based on nanoporous, composite metal carbide or metal sulfide coated membranes capable of high flux and permselectivity for hydrogen. The present invention is capable of being operated over a broad temperature range, including at elevated temperatures, while maintaining hydrogen selectivity.

BACKGROUND OF THE INVENTION

Approximately 80% of the global energy demand comes from fossil fuels, including coal, petroleum, and natural gas, and this reliance on fossil fuels is expected to increase. The combustion of fossil fuels produces CO₂, which may continue to effect climate change. As a result, a number of strategies are being explored to efficiently separate and store CO₂ in large stationary sources, such as fossil fuel based power plants, which produce over 50% of the electricity in the U.S., rather than in mobile platforms, i.e. automobiles. For example, coal can be gasified to produce synthesis gas containing mostly carbon monoxide, steam, O₂, N₂ and hydrogen. This synthesis gas can be sent to a water gas shift (WGS) reactor to convert carbon monoxide and steam to carbon dioxide and hydrogen. The hydrogen can then be separated using a hydrogen separation membrane, leaving the non-permeating CO₂ product at pressure or using the hydrogen and CO₂ for other processes. The hydrogen separation technique could be applied to many other processes including steam reformed natural gas, ammonia purge gas streams, methanol or other fuels and chemicals from synthesis gas, refinery off-gas streams, and fuel-cell power systems for transportation.

Global production of H₂ stands at about 50 million tons/year, and is increasing due to continued expansion of hydrocracking operations required by low grade fuels such as tar sands. Over 95% of H₂ is derived from fossil fuels such as natural gas or coal through processes such as steam reforming that yield the following overall reactions:

These processes proceed through CO as an intermediate, and overall conversion is limited by the equilibrium nature of the WGS reaction:

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High temperature, inorganic membrane technology is currently being investigated to perform many of the separations needed for co-generation of electric power or hydrogen from fossil fuels while simultaneously concentrating and capturing CO₂. However, the current lack of economical separation technology for these high temperature applications makes H₂ recovery unfeasible.

A method for making perfectly selective metallic membranes that are permeable to hydrogen using a palladium catalyst layer on both sides of a hydrogen permeable metal or metal alloy substrate from Group VI and Group V of the Periodic Table including vanadium, niobium and tantalum, is generally known in the art. The palladium catalyst layer allows Group VI and Group V metal membranes to be used as hydrogen separation membranes. However, at temperatures above 350° C., the palladium catalyst layer diffuses into the metal membrane and the hydrogen permeability performance decreases dramatically. Furthermore, there is a high cost associated with applying and using the palladium and palladium alloy catalysts.

Thus, there is a significant need in the energy industry and other related fields to provide an economical membrane that is permeable to hydrogen over a broad temperature range and process to purify hydrogen from contaminants as well as other compounds.

SUMMARY OF THE INVENTION

The present invention discloses the potential of molybdenum carbide to serve as stable catalysts for H₂ dissociation in high temperature membrane applications. The catalytic properties of transition metal carbides, particularly those of tungsten and molybdenum, were recognized in pioneering work by Boudart's group as discussed in J. S. Lee, S. T. Oyama, M. Boudart, *J. Catal.*, 1987, 106, 125 and incorporated by reference herein. These carbides and analogous sulfides have been pursued as substitutes for precious-metal catalysts in reactions requiring hydrogen oxidation/dissociation, such as in fuel cells or WGS reactors. Although they are not necessarily intrinsically hydrogen permeable, dissociated hydrogen readily diffuses along their surfaces. The thin layers of carbides may allow for the transport of dissociated hydrogen to the underlying metal along grain boundaries or micro-scaled defects. The carbides are non-metallic, mechanically durable, and have extremely highly melting points, all of which should make them less prone to alloying with the base metal and enable stable operation at high temperature. The proposed carbide/metal composites contain no platinum group or platinum group metals, which reduces material and process costs by orders of magnitude relative to Pd-based systems.

One aspect of the present invention will optimize the performance of novel, high temperature, surface diffusion membranes based on metal (for example, Molybdenum or Tungsten) carbides, sulfides, nitrides, bi or multiple layers of the catalysts and alloys catalysts. The hydrogen chemically adsorbs on the metal carbide, sulfide and nitride layers, and diffuses through the pores on the catalyst surface. In one aspect of the invention, these membranes contain no platinum group metals (PGMs) such as ruthenium, rhodium, palladium, osmium, iridium or platinum.

It is a further aspect of the present invention to provide a hydrogen permeable membrane that is operable over broad temperature ranges, including elevated temperatures. These temperatures are typically between about 200° C. and about 600° C.

It is another aspect of the present invention to provide the metal carbide, sulfide or nitride, or combinations thereof,

catalyst layer to various crystalline or amorphous metals or alloy substrates of various geometric configurations. In certain embodiments, these geometric configurations may include tubular, planar, non-planar and hollow fibers. In other embodiments the substrate is a body center cubic metal foil.

It is another aspect of the present invention to provide a transition metal carbide catalyst layer on dense metals from Transition Metal Groups III, IV, V and VI, including but not limited to vanadium, tantalum, niobium, and manganese. Once the metal carbide catalyst layer dissociates the hydrogen, the atomic hydrogen can diffuse through the body centered cubic (BCC) phase dense metal. The metal catalyst layer is essential for dissociating molecular hydrogen to atomic hydrogen without the use of platinum group metals.

It is a further aspect of the invention to repair pores larger than about 3 nm in the metal carbide coating.

It is a further aspect of the present invention to provide a method for applying the metal carbide, nitride or sulfide catalyst layer to the substrate. In one embodiment of the invention, the catalyst layer can be attached to the substrate using chemical vapor deposition, including RF sputtering. More particularly, the method for chemical vapor deposition can be plasma enhanced chemical vapor deposition (PECVD). Another aspect of the invention applies and tailors the final pore size of the metal carbide catalyst using atomic layer deposition (ALD) and/or pulsed PECVD. Alternatively, the metal carbide catalyst can be adhered to the substrate by physical deposition or sputtering. The metal carbide catalyst can also be applied using conventional powder processing and creating a slurry of the precursor metal oxide, which can be applied to the substrate by a variety of application methods. In other embodiments, the catalyst layer may be formed through deposition of an oxide and its subsequent conversion to a carbide, nitride or sulfide layer. In still other embodiments, the carbide, nitride or sulfide layer can be applied directly to the substrate. In still other embodiments, a combination of the conversion of an oxide layer to a carbide, nitride and sulfide layer can be used in combination with directly applying a carbide, nitride or sulfide directly to the surface of the substrate. In still other embodiments, carbide, nitride or sulfide (or combinations thereof) layers are applied to both sides of the substrate.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 illustrates a general overview of a molybdenum carbide composite membrane;

FIG. 2 illustrates a general overview of a BCC substrate with catalyst layers;

FIG. 3 illustrates SEM images of a substrate coated using pulsed PECVD;

FIG. 4 illustrates the hydrogen flux vs. square root of the partial pressure gradient, inset illustrates flux vs. feed pressure;

FIG. 5 illustrates hydrogen permeability as a function of application temperature;

FIG. 6 illustrates x-ray diffraction patterns as a function of application temperature;

FIG. 7 illustrates RMS roughness as a function of application temperature;

FIG. 8 illustrates effect on hydrogen flux over time;

FIG. 9 illustrates TEM images following hydrogen permeation testing; and

FIG. 10 illustrates energy dispersive spectroscopy results at various locations.

DETAILED DESCRIPTION

The present invention relates to a hydrogen separation membrane that does not require a platinum group metal cata-

lyst. The present invention provides a hydrogen selective membrane that is effective over a broad temperature range, including elevated temperatures, without poisoning the membrane. These hydrogen selective membranes can be very effective chemical reactors for reactions where hydrogen is a product. Examples of such uses includes, but is not limited to, use with ammonia decomposition or the WGS reaction. Removal of the hydrogen product allows the reactor to operate in a non-equilibrium mode, and conversions can exceed the equilibrium value. In the case of the WGS reaction, performing this reaction in a membrane reactor can produce both pure hydrogen and concentrated CO₂ product streams.

Referring to FIG. 1, a general overview of the molybdenum carbide composite membrane **100** for use with hydrogen separation is shown. The catalyst layer **116**, here depicted as Mo₂C, coats the porous zirconia layer **112** of a porous stainless steel substrate **108**. A gaseous mixture **128**, including H₂, enters the membrane **100**. While the H₂ **124** is able to permeate through the membrane **100**, the remaining gaseous mixture **128**, is not able to permeate through the membrane.

FIG. 2 illustrates an embodiment of a catalyst composite membrane **200**. The substrate **216** is coated on both sides with catalyst layers **212** and **228**. The catalyst layers **212** and **228** may be the same catalyst or they may be different catalysts. In some embodiments, catalyst layer **212** may be a metal carbide, metal nitride or metal sulfide catalyst layer. In some embodiments, multiple layers of a metal carbide, metal nitride or metal sulfide catalyst layer are used to comprise catalyst layer **212**. In some embodiments, catalyst layer **228** may be a metal carbide, metal nitride or metal sulfide catalyst layer and in some embodiments catalyst layer **228** may comprise multiple layers of a metal carbide, metal nitride or metal sulfide. The catalyst layers **212** and **228** are generally nanostructured and are about 2 to about 50 nanometers thick. The substrate **216** is a BCC foil. The substrate **216** material may be any BCC structured material, including but not limited to dense metal substrates from Groups III, IV, V and VI. Non-limiting examples of these substrate metals may include vanadium, niobium and tantalum and alloys thereof. In some embodiments, the substrate **216** material is a BCC foil. The substrate **216** is less than about 1 to about 75 μ m thick. Hydrogen gas **204** present on one side of the catalyst composite membrane **200** and dissociate to atomic hydrogen **208**, permeates through the catalyst layer **212** and substrate layer **216**. Optional porous layer **224** may also be included in embodiments of the present invention. The atomic hydrogen **208** recombines on the surface of the catalyst layer **228** and desorbs as molecular hydrogen gas **204**, which is then transported through the porous layer **224**. Optional porous layer **232** may also be present above catalyst layer **212**. In some embodiments, only one porous layer **224** is used. Porous layers **224** and **232** may be the same porous material or they may be different porous materials. The porous layers **224** and **232** may include but is not limited to alumina, silica, zirconia, ceria, titania and the like.

The present invention uses a metal catalyst layer, such as a transition metal carbide, transition metal nitride or transition metal sulfide catalyst on a substrate. Though metal carbide is used throughout the specification, it should be understood that a metal carbide or a metal sulfide catalyst may be used as the catalyst layer. It is an object of the present invention to apply the metal carbide to the substrate in a number of different ways. The metal carbide catalyst layer allows the hydrogen to permeate through the substrate, but unlike platinum group metals, the metal carbide catalyst layer does not poison the substrate when used at elevated temperatures. Rather, the present invention improves the temperature range

of use of the hydrogen separation membrane. Metal carbide, including Mo_2C , facilitates surface diffusion of hydrogen that is thermally activated up to about 600°C . while maintaining hydrogen permutation at elevated temperatures.

Several materials have been identified as possible substrates for the present invention. Various porous, inorganic crystalline or amorphous metals or alloy substrates may be used with the present invention. For example, SAE grade stainless steel may be used with the present invention. Additionally, porous stainless steel substrates, including AccuSep™ porous stainless steel filter media from Pall Corporation, may be used with the present invention. Other non-limiting examples of substrates may include nickel, including nickel alloys, such as Hastelloy or Inconel. Furthermore, the substrates may be coated with a porous oxide coatings, including but not limited to alumina, silica, zirconia, ceria, titania and the like. In other embodiments, the substrates are coated directly with the metal carbide catalyst layer.

Alternatively, alumina substrates may be used with the present invention, such as Anopore™ inorganic substrates. These substrates may also be coated with a porous oxide coating. In other embodiments, the substrates are coated directly with the metal carbide catalyst layer.

It is another aspect of the present invention to apply the transition metal carbides, nitrides, and sulfides on dense metals from Groups III-IV. Non-limiting examples include vanadium, tantalum, and niobium. Once the metal catalyst layer dissociates the hydrogen, the atomic hydrogen can diffuse through the body centered cubic phase dense metal. The metal catalyst layer is essential for dissociating molecular hydrogen to atomic hydrogen. These substrates may be coated with an oxide coating, then converted to a metal carbide catalyst layer or the substrates are coated directly with the metal carbide catalyst layer.

The substrates may be any geometric configuration. For example, the substrates may be tubular, planar, non-planar or hollow fibers.

The present invention also discloses a method to identify and repair large pores in the substrate to eliminate non-selective transport by viscous flow. In order to achieve selectivity, larger pores that allow transport by viscous flow need to be minimized.

Another aspect of the present invention is a method to determine if a repair of the substrate is necessary. An initial permeation test may be performed with an inert gas, including N_2 . If the permeance of the inert gas is constant over a range of feed pressures, then a repair of the substrate will not be necessary because only selective transport mechanisms are occurring. Testing can also be performed at various temperature ranges. Pure gas permeation rates with the inert gases may be measured for a range of pressure differentials (about 5 psi to about 170 psi) and temperatures ranging from about 200°C . to about 700°C . on membranes considered free of large defects based on the preliminary N_2 permeance analysis. Ideal separation factors will be computed as ratios of gas permeances (flux/ ΔP). Permeance and ideal separation factors may be compared to literature studies and flux targets to select acceptable substrates. If, however, the inert gas permeance is not constant over a range of feed pressures, the selective transport mechanisms are not occurring and repair techniques may be necessary.

The present invention provides a method to repair a substrate if the selective transport mechanisms are not occurring. Prior to the deposition of the metal oxide layer, a removable polymer template (ethyl cellulose, a polyimide, or a similar glassy polymer) is used to fill the pores in the top layer of the substrate. The polymer template fills in the pore space and

smoothes out the surface roughness. The polymer template may be applied by to the entire surface of the substrate or localized to specific locations by any suitable means. For example, the glassy polymer may be used to fill the pores of the zirconia top layer of an AccuSep™ filter. Filling the pores creates a relatively smooth surface for the deposition of the metal oxide film. The polymer template used to repair the substrate, which fills the pore structure of the substrate and acts as a template prior to the deposition of the catalyst layer, is chosen depending upon the optimum metal oxide deposition layer of the catalyst precursor. In a preferred embodiment, the glassy polymer solution is about 15% ethyl cellulose in acetone. Ethyl cellulose has a high glass transition temperature of about 133°C . and is an excellent film former. If the optimum metal oxide deposition temperature is higher than about 120°C ., a higher glass transition polymer such as a polyimide will be used as a template. The pores on the substrate are coated with enough of the glassy polymer to fill up the pores at the surface of the substrate. After the coating is applied to fill the pores at the surface of the substrate, inert gas can be used to determine if the glassy polymer has filled the holes, thereby decreasing the inert gas flow through the substrate coated with the template. The polymer layer will stay intact but may be removed by combustion in air at a suitable temperature after deposition of the oxide coating, which may be measured using Thermal Gravimetric Analysis. For example, if ethyl cellulose in acetone is used as the glassy polymer template, then it may be removed by oxidation in air at about 400°C . Other polymeric templates that can withstand higher temperatures, such as a polyimide such as Vespel™ by DuPont for example, will require a higher oxidation temperature to remove the template.

Alternatively, an inorganic template such as aluminum or cerium hydroxide can be used. An inorganic template may be preferable if the oxide layer is applied at elevated temperatures, greater than about 400°C . for example. These application temperatures prohibit the use of some polymer templates that cannot withstand these elevated temperatures. The inorganic template can be in any suitable form, including a gel. Similar to the polymeric template, the inorganic template fills the pores of the substrate. After the coating is applied to fill the pores on the surface of the substrate, inert gas can be used to determine if the inorganic template has filled the holes, thereby decreasing the inert gas flow through the coated substrate. The membrane is formed on top of the inorganic template layer. The template is removed by heating in an oxidizing atmosphere where the hydroxide is converted to an oxide.

After either the polymeric template or the inorganic template is removed, the metal oxide layer remains on the substrate, which can then converted to a carbide layer.

Once a substrate is chosen, and preprocessing is completed if it was found to be necessary, the catalyst layer may be applied. Group VI transition metals carbides, nitrides and sulfides, including molybdenum and tungsten, have platinum-group-like catalytic and adsorption properties. Additionally, molybdenum carbide membranes exhibit surface diffusion flow properties similar to those observed with platinum group membranes and the hydrogen binding energy for Mo_2C is similar to platinum and alloys of platinum group metals. It is an object of the present invention to apply a porous (about 5 nm to about 50 nm) Group VI transition metal catalyst layer to a substrate for use in hydrogen separation. These metal catalyst materials are advantageous over platinum group catalysts because they are very thermally stable (melting points exceeding about 2000°C .) and chemically stable over a wide range of conditions. (e.g. the carbide materials can be used to catalyze the WGS reaction, hydrodesulfu-

rization, hydrocarbon reforming, etc.). The hydrogen chemically adsorbs on these metal catalysts, and diffuses through the pores on the surface of the membrane.

Though molybdenum and tungsten carbide catalyst layers and compounds are discussed in detail throughout the specification, it should be understood that the present invention will be applicable to the all of the Group VI transition metals and their alloys. Furthermore, the present invention would be applicable for transition metal nitride and sulfide layers as well.

Transition metal disulfides, e.g. MoS₂, WS₂, have been shown to display similar catalytic activity to the metal carbides discussed above. Transition metal sulfides are advantageous for hydrogen selectivity because these materials are inherently resistant to sulfur poisoning and will require sulfur in the gas phase to stay in the sulfide form. Transition metal nitrides are also a feasible option for the catalyst layer.

It is an object of this invention to apply a metal carbide catalyst layer to the substrate. The application of the metal carbide catalyst to the substrate of the present invention can occur in several different ways. The metal carbide catalyst can be applied using RF sputtering for example. A novel application of the present invention utilizes plasma enhanced chemical vapor deposition (PECVD) for the synthesis of transition metal oxides, including the metal oxide precursor to the metal carbide catalyst layer of the present invention. In general, the PECVD applies a precursor to the surface of the substrate, then converts the precursor to metal carbide. The PECVD approach is advantageous because it delivers very smooth films at high deposition rates (generally, greater than about 100 nm/min) at room temperature. Additionally, since the PECVD process occurs at low temperatures, typically less than about 150° C., a polymer template may be used rather than an inorganic template to repair damaged pores in the substrate or as a template material to smooth out the surface of the substrate material prior to application of the metal oxide precursor layer.

In another aspect of the present invention, the PECVD is pulsed to behave as a self-limiting growth process (i.e. about 1 A/pulse). The pulsed PECVD of the present invention allows final pore size tailoring in the metal carbide layer of the supported substrate.

The metal catalyst layer may be applied directly to the substrate. Physical deposition of the metal catalyst layer may be deposited over a large temperature range, for example from room temperature (approximately 25° C.) to about 600° C. The substrates may be heated to their respective application temperatures and the carbide catalyst may be applied. In some embodiments, the substrate may be heated to its application temperature under vacuum and the catalyst layer may be applied.

As explained above, a chemical precursor can be used during vapor phase deposition of a transition metal oxide, carbide and/or sulfide. For both molybdenum and tungsten, there are two preferred precursors: metal carbonyls or metal halides. In one embodiment of the present invention, the precursor is a vapor at ambient conditions. Thus, the metal oxide, which acts as a co-reagent, can be applied at room temperature. Other aspects of the present invention utilize precursors that are solids at room temperature. During these conditions, the solids and vapors are introduced by sublimation into a carrier gas, which may include helium, nitrogen, argon, hydrogen and air. The reactor and/or substrate temperature must be greater than the source temperature in order to prevent precursor condensation in the reactor. The oxidizer in all cases will be O₂, while H₂ is often supplied when using the halide precursors to scavenge the ligands. Table 1 includes

examples of different precursors that may be used during the vapor deposition, though the list is not exclusive.

TABLE 1

Precursors used for the vapor phase deposition of transition metal oxides, carbides, and sulfides.			
Precursor	Phase	Delivery Method	Co-Reagents
WF ₆	Gas	Mass Flow Controller	Oxides: O ₂ , H ₂
MoF ₆	Gas	Mass Flow Controller	Oxides: O ₂ , H ₂
W(CO) ₆	Solid	Sublimes ~150° C., B.P. 175° C., Carrier Gas	Carbides: CH ₄ , C ₂ H ₂ , C ₂ H ₄ , H ₂
Mo(CO) ₆	Solid	Sublimes ~130° C., B.P. 156° C., Carrier Gas	Sulfides: H ₂ S
MoCl ₅	Solid	M.P. 194° C., B.P. 268° C., Carrier gas	

In a preferred embodiment, WF₆ and MoF₆ are the precursors for the vapor phase deposition of transition metal oxides, carbides and sulfides. To a first order, the deposition rate of PECVD is first order in precursor density, whereas the O₂ flowrate controls the oxidation state of the resulting films. The precursor flowrate can be adjusted to deliver deposition rates, generally greater than about 100 nm/min, and the O₂:precursor ratio will be generally greater than about 10 to ensure that the resulting films are fully oxidized.

To coat the substrate, a motorized rotary motion feedthrough may be added to the PECVD reactor, though it is not required. This feedthrough suspends the substrates in the middle of the plasma volume, while continuously rotating them to ensure a uniform coating. The feedthrough will be electrically grounded, providing a similar deposition environment as experienced by a planar grounded electrode. In a preferred embodiment, the weld ends of the tubular membranes may readily be attached to a source gas using compression fittings.

Smooth resulting films will be achieved as a result of the present invention. By applying a smooth film, pinholes are eliminated and pore size of the catalyst layer is tightly controlled. The oxides deposited by PECVD are very smooth, with typical RMS roughness values of about 1 nm on smooth substrates (i.e. Si, glass). In one aspect of the invention, an inorganic substrate is used, such as a stainless steel substrate. The nominal pore size on the zirconia coated stainless steel membranes is about 70 nm and a smooth metal carbide catalyst is applied to the substrate. In the event that the smoothness of the porous oxide coated substrate is unsatisfactory, a glassy polymer template will be employed to smooth the surface of the porous oxide coating prior to deposition as described in greater detail above with regard to the substrate. In one aspect of the invention, in order to promote a smooth and even catalyst layer, a film layer can be formed on the surface of the substrate by applying a coat of a glassy polymer template solution. The polymer template will be determined depending on the optimum metal oxide deposition temperature. The porous oxide coating is coated with enough of the glassy polymer template to fill up the pores on the surface. After the coating is applied to fill the pores on the surface of the coating, inert gas can be used to determine if the glassy polymer template has filled the holes, thereby decreasing the inert gas flow through the porous oxide coating. The polymer template will stay intact but may be removed by combustion in air at a suitable temperature after deposition of the oxide coating, which may be measured using Thermal Gravimetric Analysis. In a preferred embodiment, the glassy polymer template solution is ethyl cellulose in acetone.

Since the PECVD synthesis method generally occurs at low temperatures, the polymer layer will stay intact but may be removed by oxidation in air at about 400° C. after deposition of the oxide coating. At this point, the dense metal oxide films, e.g. MoO₃, WO₃, will be converted to nanoporous, generally about 2 nm ≤ d_p ≤ about 3 nm metal carbide, e.g. Mo₂C, W₂C, films using literature temperature programmed reaction (TPR) methods in a hydrocarbon/H₂ atmosphere. The TPR conditions necessary to convert the dense metal oxides to nanoporous metal carbides may be optimized using the metal oxide materials previously applied to the substrate and controlling the TPR conditions. The TPR conditions of about 80% H₂ in gaseous phase hydrocarbon, for example, a binary mixture of methane, acetylene or butane, at a heating rate of about 0.5° C./min to about 1° C./min with a maximum temperature of about 927° C. Upon reaching the maximum temperature, the substrate will be cooled in pure hydrogen and then passivated in about 1% O₂, or other oxidizing gas including carbon dioxide, in a noble or inert gas such as Argon, Nitrogen or Helium for example.

There are several advantages to the above described procedure. For example, because the molar volume of Mo₂C is smaller than the molar volume of MoO₃, micropores form as the oxide transforms to the carbide. Also, the MoO₃ is converted to Mo₂C without having metallic Mo as a reaction intermediate. Metal sintering is also avoided using this method, and unsupported catalysts can be prepared with very high surface areas (generally, greater than about 100 m²/g), and corresponding pore sizes are below about 3 nm, more preferably between about 1 and about 3 nm. The pore size can be engineered or tailored by modification of the TPR conditions for the production of Mo₂C and the TPR conditions may be monitored and controlled in situ using quadrupole mass spectrometry (QMS). Water is the main byproduct of the reduction process. Monitoring the evolution of the water byproduct provides a measure of both the rate and extent of the carburization process and optimization of the TPR process conditions (heating rate, gas composition, etc.).

In another aspect of the present invention, reactive plasma discharges are used to deposit thin films and modify surface properties of substrates. In these non-equilibrium discharges, electromagnetic energy is selectively delivered to electrons, which in turn are heated to several eV (about 10,000 K-about 50,000 K). However poor elastic coupling between the electrons and the relatively heavy gas molecules allows the latter to remain at ambient conditions. As a result plasma allows activated chemical processes to occur readily at low temperature without impurities.

Another important aspect of PECVD is its high deposition rate; transition metal oxides, such as WO₃ and V₂O₅, have been deposited at rates generally greater than about 100 nm/min, which is critical for efficient, industrially acceptable, synthesis of the micron-scale layers required in the formation of hydrogen separation membranes.

Though atomic layer deposition (ALD) may be used for self-limiting growth, the pulsed PECVD process may also be used as an alternative. The self-limiting nature of pulsed PECVD allows for highly conformal deposition on non-planar substrates. Pulsed PECVD has an advantage over ALD in that this conformal deposition can be achieved at high rates and low temperature and can be tuned depending on the applications. FIG. 3 shows the two extremes that can be obtained. FIG. 3a is a high aspect ratio trench that was completely filled with Al₂O₃ using pulsed PECVD. Note that the remaining hole is a reflection of notches in the original trench structure, further confirming the conformal nature of the process. FIG. 3b shows a coating with no conformality, where the

substrate is an anodized alumina support (Anopore™) with vertical pores that are nominally about 200 nm in diameter. A dense layer of SiO₂ was deposited over the porous structure, with little deposition in the pores themselves. This dynamic range of conformality may be obtained by simply varying the operating conditions of the pulsed PECVD process.

Chemical vapor deposition (CVD) of MoO₃, WO₃, and mixed transition metal oxides has been accomplished using the same precursors described above in Table I to form the catalyst layer of the membrane. The principal difference is that CVD requires higher temperatures (about 100° C. to about 400° C.), so it may be detrimental to the polymer templates, though an inorganic template material may be used. Alternatively, a polymeric template that may withstand temperatures above about 400° C., may be used.

Another aspect of the present invention applies the metal carbide catalyst layer using a precursor slurry or via chemical bath deposition. The solution comprises the metal oxide, an alcohol, a surfactant and a hydrocarbon binder. The substrate is coated in the metal carbide catalyst by, for example, dipping, spraying, painting, pouring or rolling. The coated substrate is subjected to high temperatures so the metal oxide can be converted to carbide using carburization procedures known in the art. For example, the MoO₃ compound can be converted to the sulfide by reacting it with a mixture of H₂ and H₂S between about 500° C. and about 650° C. Other synthetic methods for the synthesis of MoS₂ from MoO₃ are reviewed by P. Afanasiev, *Comptes Rendus Chimie.*, 11 (2008) 159-182, incorporated herein by reference.

In still other aspects of the present invention, the metal catalyst layer may be applied directly to the surface of the substrate or to a porous layer using vapor deposition techniques, including sputtering, CVD, PECVD or by solution growth through use of slurries or chemical bath deposition.

Another aspect of the present invention allows the hydrogen separation membrane be assessed in situ. After deposition of a given amount of material, the integrity of the hydrogen separation membrane can be assessed in situ by supplying an inert gas to the membrane interior and testing the flux as a function of inlet pressure. If the permeance of the inert gas is insensitive to a change in pressure, then the viscous flow is negligible and repair of the membrane is not necessary.

In another aspect of the invention, the membranes are annealed following the deposition of the metal carbide films to create porosity, strength and adhesion between the substrate and the metal carbide catalyst. The metal carbide catalysts can typically be annealed between about 400° C. to about 1000° C.

In another aspect of the invention, the porous metal carbide layers will be functionalized with a thin (about 1 nm) layer of sulfide deposited by PE-ALD and/or pulsed PECVD. This sulfur layer may provide benefits, including the prevention of sulfur poisoning.

The membranes may be used in a variety of applications. For examples, the membrane may be incorporated into a reforming or WGS reactor, the removal of products can drive reactions (1-3) described above toward complete conversion.

The flux of H₂ through metal membranes generally follows Sievert's law:

$$J = -D_H K_s (P_{H_2, Feed}^{1/2} - P_{H_2, Permeate}^{1/2}) \quad (4)$$

where J is the flux of molecular hydrogen, D_H is the diffusion coefficient, K_s is the solubility constant, and P_{H₂} is the partial pressure of H₂. The square root pressure dependence arises in these systems when the rate of H₂ dissociation and recombination on the surfaces is much faster than transport through the bulk. This is the case for all but the thinnest palladium

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membranes, and for most BCC-metal membranes at temperatures above 400° C. Deviations from Sievert's law are most often observed when the surface is poisoned, and the flux becomes limited by H₂ dissociation.

EXAMPLES

Example 1

Thin layers of Mo₂C were applied to both sides of 50 μm thick vanadium substrates by sputtering. All substrates tested had zero detectable flux of helium up to transmembrane pressures of ΔP=690 kPa, which indicates that transport via pinholes is negligible in these structures. A control substrate with no Mo₂C catalyst layers also had no hydrogen flux, with the detection limit being $5.9 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ for both He and H₂. This demonstrates that the Mo₂C catalyst layer is solely responsible for hydrogen dissociation. All membranes coated with Mo₂C layers displayed detectable hydrogen transport, with the most permeable material to date shown in FIG. 4.

The carbide-coated vanadium films showed poor correspondence to Sievert's law, having a linear relationship with pressure, rather than P^{1/2} as shown in FIG. 4. This suggests that the catalyst layer is limiting the rate of hydrogen transport in these membranes, due to the lower activity of Mo₂C compared to materials such as Pd. To further test this argument the structure of the carbide layers were varied by changing the sputtering conditions as explained in Example 2.

Example 2

FIG. 5 illustrates the hydrogen permeability as a function of temperature for carbide-coated vanadium membranes fabricated at selective temperatures, compared with permeability data for bulk palladium. FIG. 5 compares the temperature dependence of H₂ permeability for Pd with four composite carbide membranes whose catalyst layers were deposited at different temperatures. Although all the membranes have permeabilities significantly lower than vanadium's theoretical maximum, the membranes sputtered at about 200° C. and about 600° C. are comparable to permeability of palladium membranes, particularly at higher temperatures. The observed trend of higher permeability with increased temperature provides additional support that the carbide layer limits hydrogen transport, as flux through bulk vanadium drops with temperature due to decreased hydrogen solubility in the lattice.

The H₂ separation performance observed in FIG. 5 was correlated with changes in crystal structure and surface morphology of the sputtered carbide.

Example 3

FIG. 6 illustrates images demonstrating the effect of temperature on Mo₂C film properties. The properties of as-deposited Mo₂C as a function of sputtering temperature are shown in FIG. 6. The X-ray diffraction (XRD) patterns obtained from as-deposited films as a function of sputtering temperature are compared with literature values in FIG. 6. The film deposited at room temperature (RT), approximately 25° C., displays the cubic phase (JCPDS 15-0457), though the peaks are broad and low-intensity, suggesting that the material is nanocrystalline and/or substantially disordered. Films deposited at about 200° C. retain the cubic structure, but the degree of crystallinity is dramatically improved as evidenced by the increased intensity and reduced width of the diffraction peaks. At about 400° C. the crystalline nature is lost, while a

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further increase in substrate temperature to about 600° C. suggests that the films begin to adopt the orthorhombic crystal structure (JCPDS 79-0744).

Example 4

The deposition temperature was also found to have a profound impact on film morphology, as shown by the atomic force microscopy (AFM) images presented in FIG. 7. The films displaying the cubic phase at RT and about 200° C. display a nanocrystalline morphology that is quite smooth, with a root mean square (RMS) roughness of about 1 nm. The surface of the film deposited at about 400° C., which has no discernable crystal structure, is featureless and ultrasmooth. At about 600° C. the appearance of the orthorhombic phase coincides with the return of a nanocrystalline morphology with significantly larger features and a RMS roughness of about 10 nm. The observed evolution of microstructure with substrate temperature is qualitatively consistent with Thornton's zone diagram for sputter-deposited coatings. Comparison of FIG. 5 and FIG. 6 suggest that the carbide morphology plays an important role for H₂ transport in this system. The highest permeability was obtained at about 200° C. and about 600° C., which displayed the highest degree of crystallinity and surface structure, respectively. In contrast, the permeance was significantly lower in samples fabricated at RT and about 400° C. which had little discernible crystal structure or surface features. These findings support the hypothesis that grain boundaries play an important role in hydrogen transport through these layers. It is expected that the performance of these systems can be further enhanced by improving the microstructure and/or reducing the thickness of the carbide layers.

Example 5

A critical issue with BCC membranes is the temperature stability of the catalyst layer. A vanadium foil coated with Mo₂C membrane was tested for over 160 hours at elevated temperature (≥about 600° C.) and showed no loss of hydrogen permeability as shown in FIG. 8. In fact, the hydrogen flux may actually improve slightly with time when held at high temperature. By comparison, a palladium-coated vanadium membrane would be expected to lose 50% of its hydrogen permeability within 90 minutes of exposure to hydrogen at about 700° C. This indicates that the carbide catalyst is not reduced to metallic molybdenum which would be expected to alloy with the bulk vanadium. FIG. 9 displays a cross-section transmission electron microscopy (TEM) image of a membrane after permeation testing. This particular carbide layer was deposited at 600° C. The interface between the carbide layer and vanadium remains very sharp after extensive testing at elevated temperatures. The composition and structure of these layers were further interrogated using selected area diffraction (SAD), convergent beam electron diffraction (CBED), and energy dispersive spectroscopy (EDS). The carbide layer is on the order of approximately 65 nm thick, and appears to be quite dense. The inset at the upper right of FIG. 9a is the CBED image taken with the electron beam focused at the center the carbide layer. The regular array reflects the crystallinity of this phase, and indexing of the reflections confirms that it is the orthorhombic phase of molybdenum carbide, consistent with the XRD pattern obtained from the as-deposited layer as shown in FIG. 6. There is significant roughness in this layer with individual features on the order of about 10 nm, again consistent with the morphology observed by AFM in the as-deposited layers as shown in FIG. 7. The

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presence of grain boundaries are apparent in the high resolution image in FIG. 9b, supporting their important role in hydrogen transport. FIG. 9a shows a 275,000 $\times$ magnification cross-sectional TEM image of the vanadium foil coated with Mo₂C. Insets in FIG. 9a shows selected area and convergent beam diffraction images obtained from the vanadium and carbide layers respectively. FIG. 9b shows a detailed view of the boxed segment of FIG. 9a at 1,000,000 $\times$ magnification. Note that platinum was deposited after testing as part of sample preparation using a focused ion beam.

The SAD pattern obtained from the vanadium region displays the expected cubic structure, and the extracted d-spacing confirms that it is the BCC phase. There is a notable difference in morphology in the vanadium layer directly adjacent to the carbide layer, and the material far from the interface. The interface region appears to have undergone some form of recrystallization. This is not a result of TEM sample preparation. This may be due to damage resulting from the Ar ion bombardment treatment used to remove the native oxide.

Example 6

Energy dispersive spectroscopy (EDS) was used to examine the composition at various positions in the vanadium-Mo₂C sample. The EDS spectrum shown in FIG. 10 obtained with the electron beam focused on the carbide layer showed mostly molybdenum as well as small amounts of both vanadium and platinum, which reflects the spatial resolution of the instrument. FIG. 10a illustrates a spectrum from the molybdenum carbide layer, FIG. 10b illustrates a spectrum from the vanadium layer near the carbide layer and FIG. 10c illustrates the vanadium layer far from the interface. Note that in FIGS. 10a-10c, the Cu signal derives from the sample holder. In addition the weak peak at ~ 1.8 keV labeled W is likely not tungsten, as none of the high energy peaks associated with tungsten are present. This energy level also corresponds to Si, and being present at the same intensity in each spectrum it is attributed to background contamination in the system. The EDS spectrum obtained from the position of the vanadium SAD pattern displayed no molybdenum and contained only peaks associated with V, and was identical to spectra obtained from bulk vanadium taken far from the carbide interface as shown in FIG. 10b and FIG. 10c. These nanoscale characterization techniques provide further confirmation that negligible interdiffusion occurs between these two materials under these conditions.

The maximum hydrogen flux demonstrated to date in this study is already at 30% of the U.S. Department of Energy 2015 goal, while meeting requirements with respect to selectivity. As discussed above, further improvement in the structure of the catalyst is expected to increase the overall permeability of hydrogen in these systems. Through further improvements to the catalyst layer, optimization of the bulk BCC metal's transport properties, and/or reducing the overall membrane thickness, it is expected that this material system will produce highly competitive, cost-effective membranes for high temperature hydrogen separation.

Example 7

Cold-rolled vanadium foils 50.8 micron in thickness with 99.8-99.9% purity were purchased from ESPI Metals and cut into circular samples, each 1.19 cm in diameter. As received vanadium foils contain a layer of native oxide, which hinders hydrogen transport. This layer was removed by an Ar ion sputter treatment at a pressure of 25 millitorr and 100 watts for five minutes at room temperature, which produced a DC

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bias voltage of 300 ± 1 volts on the substrate. The foils were then heated to their respective sputtering temperatures under vacuum. Mo₂C catalyst layers were deposited directly onto the clean vanadium surface without breaking vacuum by RF sputtering (AJA Orion) in Ar at 5 mtorr using 100 W of power. All films were deposited for 30 minutes, producing films ~ 65 nm in thickness. The cleaning and sputtering process was performed on both sides of the foil to facilitate dissociation upstream and recombination downstream. Carbide was simultaneously deposited onto vanadium foils and silicon wafers, and the latter were used to facilitate XRD and AFM characterization.

XRD (Siemens Kristalloflex 810) was performed using a Cu K α radiation, and films were scanned over a range of $2\theta = 15-65^\circ$ using a step size of 0.05° . AFM (Digital Instruments Nanoscope III) images were obtained in tapping mode. TEM sample preparation employed the focused ion beam capabilities of a field emission scanning electron microscope (FESEM, FEI Quanta 3D FEG Dual Beam), while imaging was conducted on a FEI Tecnai T20 TEM. Selected area diffraction studies and energy dispersive spectroscopy were performed using a Philips CM200 TEM.

Membranes were permeation tested by mounting in $\frac{1}{2}$ " SwagelokTM VCR fittings. The gaskets used were silver-plated nickel to provide a leak-free seal at the elevated temperatures studied while reducing possibility of hydrogen transport through the seals. This created an effective membrane surface area of 0.93 cm^2 . A filter gasket with a nominal particle rejection size of 10 microns was placed on the permeate side of the membrane to prevent excessive mechanical distortion of the thin foil under high feed-side pressures while providing negligible resistance to flow. The test fixture was mounted in a furnace, and heated under the flow of ultra high purity (UHP) He at $1^\circ \text{ C./minute}$ to the base test temperature of 600° C . This prevents low-temperature hydrogen embrittlement of the vanadium bulk, while protecting against destructive oxidation. The membrane was then characterized by single-gas permeation experiments using industrial-grade hydrogen and UHP helium as described in Table 2. The permeate side of the membrane was maintained at atmospheric pressure, locally approximately 82 kPa, and no sweep gases were used during permeation testing. Permeate flows were measured using a soap film meter.

TABLE 2

Order and conditions of experiments			
Experiment	Elapsed time (hours)	Temperature ($^\circ \text{ C}$.)	Feed pressure (gauge, kPa)
Flux stabilization	0-40	600	138
Thermal cycling	40-48	600-700	138-690
Stability testing	48-168	600	690

For clarity, the following is a list of components and the associated numbering used in the drawings.

#	Components
100	Coated membrane
108	Porous stainless steel substrate
112	Porous zirconia layer
116, 212, 228	Catalyst layer
124, 204	Hydrogen gas
128	Mixture
200	Catalyst composite membrane

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-continued

#	Components
208	Atomic hydrogen
216	Substrate
224, 232	Porous layer

While an effort has been made to describe various alternatives to the preferred embodiment, other alternatives will readily come to mind to those skilled in the art. Therefore, it should be understood that the invention may be embodied in other specific forms without departing from the spirit or central characteristics thereof. Present examples and embodiments, therefore, are not to be considered in all respects as illustrative and not restrictive, and the invention is not intended to be limited to the details given herein.

What is claimed is:

1. A method for making a hydrogen separation membrane, comprising:

providing an inorganic substrate;

applying at least one transition metal catalyst layer to said inorganic substrate, wherein the hydrogen separation membrane does not include a platinum metal group material; and

determining if a repair of said inorganic substrate is necessary by performing a permeation test with an inert gas.

2. The method of claim 1, wherein said inorganic substrate is selected from the group consisting of an inorganic porous substrate and a body center cubic dense metal substrate.

3. The method of claim 2, wherein said inorganic substrate is said body centered cubic dense metal substrate and wherein said body centered cubic dense metal substrate is selected from the group consisting of vanadium, tantalum, niobium, combinations thereof and alloys thereof.

4. The method of claim 1, wherein said transition metal catalyst layer is selected from the group consisting of a transition metal carbide, a transition metal nitride, a transition metal sulfide and combinations thereof.

5. The method of claim 1, wherein said transition metal catalyst layer comprises a transition metal selected from the group consisting of a molybdenum, tungsten and combinations thereof.

6. The method of claim 1, wherein said transition metal catalyst layer is applied at a temperature between about room temperature and about 600° C.

7. The method of claim 1, further comprising coating said substrate with a polymer material to repair oversized pores on a top surface of said inorganic substrate.

8. The method of claim 1, further comprising a porous layer, wherein said porous layer is a material selected from the group consisting of an alumina, a silica, a zirconia, a ceria, a titania and combinations thereof.

9. The method of claim 1, wherein the at least one transition metal catalyst layer is applied by a vapor deposition method.

10. The method of claim 9, wherein the vapor deposition method is selected from the group consisting of sputtering, chemical deposition and plasma enhanced chemical vapor deposition.

11. The method of claim 2, wherein said inorganic substrate is said body centered cubic dense metal substrate and wherein a thin film of said body centered cubic dense metal substrate is deposited on a porous support layer.

12. The method of claim 1, wherein the at least one transition metal catalyst layer is applied by solution deposition.

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13. A method for applying a transition metal catalyst layer to an inorganic substrate to form a hydrogen permeable membrane, comprising:

providing an inorganic substrate;

applying a transition metal precursor to said inorganic substrate, wherein the transition metal precursor is a Group VI transition metal selected from the group consisting of molybdenum, tungsten and alloys thereof; and converting said transition metal precursor to a transition metal catalyst layer, wherein the hydrogen permeable membrane does not contain a platinum metal group material, and wherein a thickness of the transition metal catalyst layer is between about 2 nanometers to about 50 nanometers.

14. The method of claim 13, further comprising determining if a repair of said substrate is necessary by performing a permeation test with an inert gas.

15. The method of claim 13, further comprising coating said substrate with a polymer material to repair oversized pores on a top surface of said substrate.

16. The method of claim 15, wherein said polymer material is removed by oxidizing said substrate in air having a temperature of at least about 400° C.

17. The method of claim 13, further comprising coating said substrate with an inorganic material to repair oversized pores on a top surface of said substrate.

18. The method of claim 13, wherein a top surface of said substrate is a porous oxide coating.

19. The method of claim 18, wherein said porous oxide coating is selected from the group consisting of an alumina, a silica, a zirconia, a ceria, and a titania.

20. The method of claim 13, wherein said metal precursor is selected from the group consisting of a WF_6 , a MoF_6 , a $W(CO)_6$, a $Mo(CO)_6$ and a $MoCl_5$.

21. A hydrogen separation membrane comprising, an inorganic substrate, wherein said inorganic substrate is selected from the group consisting of a porous inorganic substrate and a body centered cubic metal substrate; and a transition metal catalyst layer deposited on two sides at a thickness of between about 2 nanometers to about 50 nanometers of said inorganic substrate, where the transition metal is a Group VI transition metal selected from the group consisting of molybdenum, tungsten and alloys thereof.

22. The hydrogen separation membrane of claim 21, wherein said inorganic substrate is said porous inorganic substrate, wherein said porous inorganic substrate is a stainless steel material.

23. The hydrogen separation membrane of claim 22, wherein said stainless steel material is coated with a porous oxide coating is selected from the group consisting of an alumina, a silica, a zirconia, a ceria, and a titania.

24. The hydrogen separation membrane of claim 21, wherein said Group VI transition metal is selected from the group consisting of a molybdenum and a tungsten.

25. The hydrogen separation membrane of claim 21, wherein said body centered cubic dense metal substrate is a foil.

26. The hydrogen separation membrane of claim 21, wherein said transition metal catalyst is a transition metal sulfide.

27. The hydrogen separation membrane of claim 21, wherein said transition metal catalyst is a transition metal nitride.

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28. The hydrogen separation membrane of claim **21**, wherein said transition metal catalyst is a transition metal carbide.

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