CONF-9710158--

LA-UR- 97-3968

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Author(s):

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TEMPERATURE HYDROGEN MEMBRANES

Submitted to:

The 1997 Fifteenth Annual Membrane
Technology Separations Planning
Conference
Newton, MA
Oct. 27-19, 1997

1998 0327 096

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Form 836 (10/96)

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ADVANCING THE TECHNOLOGY BASE FOR HIGH TEMPERATURE HYDROGEN MEMBRANES

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High purity hydrogen is a critical component for at least two major industrial processes: 1) the refining of conventional steels and raw pig iron into low carbon steels and high purity iron used for high performance magnets in motors, generators, alternators, transformers, and etc.; and 2) refining metallurgical grade silicon to the high-purity, polycrystalline silicon used in fabricating single crystal silicon wafers for semiconductor manufacturing. In the process of producing low carbon iron products, CO and CO_2 impurities prevent efficient removal of the carbon already in the raw iron. In the refining of metallurgical grade silicon, the presence of any impurity above the part-per-million level prevents the ultimate fabrication of the large scale single crystals that are essential to the semiconductor device. In a lesser magnitude role, high quality hydrogen is used in a variety of other processes, including specialty metals refining (e.g., iridium, osmium, palladium, platinum, and ruthenium) and R&D in areas such as organic synthesis and development of certain types of fuel cells. In all of these applications, a high-temperature hydrogen membrane can provide a method for achieving a very high purity level of hydrogen in a manner that is more economical and/or more rugged than existing techniques.

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The primary consumers of bulk amounts of hydrogen are the companies involved in refining petroleum to high grade, low emission fuels and the companies involved in synthesizing ammonia for the fertilizer market. These consumers account for over 97 percent of the market for hydrogen, as well as over 60 percent of the production of hydrogen. In the petroleum refining industry, hydrogen is primarily used for hydrotreating of naphtha distillates to remove sulfur, nitrogen, and other heteroatom impurities. The result is a fuel that produces lower SO_x and NO_x when burned in automobile engines, fuel oil heaters, and etc. This route to reducing overall hazardous emissions is a key element of the US national strategy to improve air quality and to meet international agreements for reducing acid rain generating emissions. In the fertilizer industry, the initial step in synthesizing essentially all nitrogen based fertilizer chemicals is the synthesis of ammonia. These fertilizers are a key ingredient to the overall productivity of US agriculture.

In the electronics industry, hydrogen is used to purify metallurgical grade silicon (roughly 98% pure silicon) to the high purity electronics grade polycrystalline silicon (less than 1 ppm of total impurities) required for integrated circuit fabrication. (Metallurgical grade silicon is produced from silicon oxides via reduction by carbon black or coke.) Purification is accomplished by reacting metallurgical silicon with HCl to form $SiHCl_3$, purifying the $SiHCl_3$ by fractional distillation, and reacting the $SiHCl_3$ with H_2 to deposit high purity polycrystalline silicon. Because impurities must be kept well below the parts per million level, high purity hydrogen is required for the last step. Electronics uses of silicon account for a small but very important fraction of total silicon use. (Most silicon is used in producing steels and other alloys.) Recent surveys indicate that use of all forms of industrial gases by the electronics industry totaled just over $1B in 1995. The majority of this consumption was of liquid nitrogen. Estimates are that hydrogen use comprised around 20 percent of this total for a market value in this market segment of nearly $200M/year.[1]

A number of technologies are being pursued as alternatives to current combustion based energy sources for utility power generation and transportation. All of these technologies are based on fuel cells that require hydrogen as the fuel. In most designs for commercially operating systems based on fuel cells, the hydrogen is formed in-situ in the fuel cell from either natural gas (for utility power applications) or methanol (for transportation applications). End user of these fuels have stated that use of these fuels is essential to the commercial viability of fuel cells due to the existing infrastructure for fuel distribution. As a result such fuel with in situ hydrogen formation require compact, efficient, low energy methods for purifying hydrogen.

The value of hydrogen increases with purity level. The technologies currently in use for purifying hydrogen vary with the end-use industry. In general, the technologies can be grouped as those primarily used by high purity hydrogen consumers and those used in the bulk production/consumption of hydrogen. Technologies in high purity applications include electrolysis, polymer membranes, and conventional palladium foils.

The electrolysis method consists of an electrical cell that applies voltage to water between two electrodes. The electrical current dissociates the H_2O molecules into H_2 and O_2 gas molecules. The electrodes typically are palladium metal or solid polymer electrolyte. An alkaline salt (e.g., KOH) is usually added to improve current carrying by the water. A wide variety of commercial systems exist and all achieve >99.9% hydrogen. The residual impurity in electrolysis hydrogen is oxygen; some electrolysis systems include a hot metal reactor for the hydrogen that removes this oxygen to achieve even higher purity. This approach is very energy intensive, requiring about 4.5 kW-hour to produce 1 m^3 of hydrogen.

A variety of polymer membrane systems have been developed for hydrogen purification. The most common technique is to use membranes made of aromatic polyaramide, polyimide, polysulfone, and cellulose acetate supported as spiral wound hollow-fiber modules. In these modules, the synthesis gas enters the core of the hollow fiber. As the synthesis gas passes down the length of the fiber, hydrogen diffuses through the wall to the tube containing the fiber. Pure hydrogen (typically ~99%) is collected from the containment tube and the impurities (with some amount of waste hydrogen) is collected from the core of the fiber.

A palladium-based hydrogen purification system was developed in 1965 by Union Carbide. This industrial system had an operating capacity of 1,130,000 m^3/day of hydrogen produced at a purity of >99.9%. In this system, hydrogen molecules (H_2) are absorbed at the surface of the palladium, are dissociated by the palladium to hydrogen atoms; the atoms diffuse through the metal foil and are recombined to form molecules on the other side. While the Union Carbide system functions quite well, it does not appear to be commonly used for large scale operations. Smaller scale units based on this technology are reported to be common for cases where purity of >99.99% are required.

In the large-scale production of hydrogen for petrochemical processing and ammonia production, the production process starts with the formation of synthesis gas -- a mixture of hydrogen and CO/CO_2 formed either from steam reforming of natural gas or partial oxidation of a hydrocarbon feed stream such as naphtha and refinery residual oils or coal. There are three techniques commonly used to purify the hydrogen from this synthesis gas, pressure swing adsorption (PSA), cryogenic purification, and catalytic purification.

The PSA process is one of the most common techniques used for high volume purification of hydrogen. In this method, synthesis gas is passed over an adsorbent material, usually a molecular sieve, and the impurities (predominantly CO, CO_2, and residual water but also some amount of sulfides and chlorides) are adsorbed on the surface of the molecular sieve material. Depending on the number of stages of molecular sieve that are used, hydrogen purity ranging from

90% to over 99.9% can be achieved. The sieve material is regenerated by pumping to a low pressure. The off-gas from the sieve is hydrogen rich; it is feed as fuel to the water heaters for the steam reformer, thus providing almost 90% of the energy required for the reformer.

Cryogenic separators strongly resemble conventional air separation apparatus with synthesis gas being the working gas. The synthesis gas is compressed and then expanded through a specially designed nozzle/turbine apparatus. Joule-Thompson cooling occurs during expansion; the motive force created in the turbine drives the up-front compressor. The cooled gas is recirculated 1) to provide cooling for input synthesis gas, and 2) to be compressed again for further expansion cooling. Since all of the impurities have higher boiling points than liquid hydrogen, they condense and are removed from the flowstream. In some designs, water, CO_2, and H_2S are removed from the flowstream prior to cryogenic purification to prevent fouling of the apparatus by frozen material. Cryogenic systems achieve purity of 90% to 99% depending on operating conditions. They are most energy efficient at the lower end of this range and can achieve 90%-95% energy recovery at a purity of ~90%.

The catalytic purification technique also is used with hydrogen produced from synthesis gas. The technique consists of a series of chemical and physicals steps that remove those impurities that are harmful in the ultimate use of the hydrogen. In short, the system consists of a series of reactors. First, the raw synthesis gas is purified of any residual sulfide and chloride impurities via adsorption on hot metal. Second, the CO in the gas is converted to CO_2 using a Fe-Cr catalyst. Next, the gas is scrubbed of CO_2 using a solvent such as water or hot potassium carbonate. Finally, any traces of residual CO and CO_2 are converted to methane using a Ni catalyst. The final gas stream is only on the order of 98%-99% pure. However, the residual impurity is methane that has little effect on ammonia synthesis and certain other uses for bulk hydrogen.

Table 1. Overview of US Hydrogen Production Capabilities

Characteristic (units of measure)	Value
1995 Production Volume (millions of cubic feet)	352,000
Volume Consumed at Point of Production (million cubic feet)	213,000
Volume Shipped Off-site (million cubic feet)	138,000
1995 Value of Shipments ($M)	311
Sources for bulk hydrogen -- percent production from	
Natural gas/petroleum	77%
Coal	18%
Water electrolysis	4%
All other routes	1%
Cost ($ per 100 m^3) for hydrogen production from	
Natural gas	7.19
Petroleum	11.15
Coal	15.46
Water electrolysis	22.63

The demands on hydrogen and hydrogen purity levels are increasing because of several factors. To meet increasing requirements for energy efficiency and warranty operations, manufacturers of electric motors, alternators, and generators are turning towards higher performance permanent magnets. Achieving higher performance requires more precise control of, and in many designs the overall reduction of, impurities in the iron or steel that reduce magnetic permeability. This, in turn, translates into a demand for increasing purity of all raw materials, including the hydrogen, used in making the desired magnet metal from the raw iron from the blast furnace. As this trend makes the existing purification approaches less effective, it creates an increased market need for alternative high purity hydrogen separation strategies. To respond to increased levels of chip integration, decreased element size, and increased production rates, the semiconductor industry is moving towards production of larger silicon substrates. Forming larger crystals of silicon demands higher purity starting materials of the SiH_3Cl. This in turn translates to higher purity requirements on the hydrogen gas in the reduction step. The result is an increasing attractiveness of technologies that can achieve extreme levels of purity.

Also, there are several regulatory issues that impact the potential for increased hydrogen use. The key regulations that are currently driving developments related to hydrogen markets are the following:

CLEAN AIR ACT AMENDMENTS OF 1990. This legislation requires use of reformulated gasoline in designated areas and requires overall reduction in the nitrogen and sulfur emissions from automobiles in general. This legislation is driving the increased use of hydrogen to produce higher quality fuels from petroleum. It has been the key issue that resulted in the market trends noted for bulk hydrogen consumption.

ENERGY POLICY ACT OF 1992. This Act specifies minimum purchases of alternative fuel vehicles by Federal agencies and mandates the acquisition of such vehicles by State and local governments. This legislation is key to the expanding market for alternative fuel vehicles and will help to sustain this market until fuel cell powered vehicles become commercially viable.

ALTERNATIVE MOTOR FUELS ACT OF 1988. This legislation directs Federal agencies to administer programs that encourage the development of alternative fuels and the production of alternative fuel vehicles. This legislation is key to the expanding market for alternative fuel vehicles and will help to sustain this market until fuel cell powered vehicles become commercially viable.

These regulations and others have caused a flurry of activity in fuel cell development. In the area of transpiration the proton exchange membrane fuel cells (PEMFC) seems to be the most promising. Most electric vehicle projects employing fuel cells use PEMFC technology that requires hydrogen as the fuel. While the vehicles currently use pressurized hydrogen as fuel for demonstration purposes, developments are underway exploring use of methanol and other

hydrocarbons as fuel by means of incorporating reformer units in tandem with the fuel cell. These reformer units require compact hydrogen purification devices for efficient operation of the fuel cell.

Table 2. Fuel Cell Vehicle Demonstration Projects

Demonstration Project	Key Characteristics
Daimler-Benz NECAR II	Employs PEMFC power systems from Ballard Power Systems; 25kW power source to drive a minivan
Chicago Transit Authority	Demonstration project consisting of three 40-foot buses using 200kW PEMFC technology provided by Ballard Power Systems
Vancouver BC Transit Authority	Demonstration project consisting of 3 buses using PEMFC technology provided by Ballard Power Systems
USDOE Fuel Cell/Battery Hybrid Vehicle	Methanol fueled PAFC plus batteries in a 20 passenger bus; design is 1/2-scale to ultimate production design

A new multilayer metal membrane developed at Los Alamos National Laboratory has demonstrated hydrogen purification for efficient fuel cell operations (Figure 1). The high performance and low palladium loading makes this membrane a promising solution for a compact, lightweight, hydrogen, purification system. Details of the membrane fabrication can be found elsewhere.[2]

The long term performance of this membrane must be properly addressed because the membrane must be able to withstand long periods of operation without degradation. So far, the flow rate as a function of time in a 575 hour test is shown in Figure 2; this experiment was run at a membrane temperature of 300°C, feed pressure of 600 torr (ambient pressure in Los Alamos, NM), permeate pressure of 17 torr, a hydrogen flow rate of 100 sccm and an Ar flow rate of 35 sccm. The flow rate per area of membrane was stable at 7.78 sccm per cm^2 which is a low flow rate for this membrane system. However, that value corresponded to an 84% efficiency, i.e., 84% of the hydrogen in the feed stream was transported across the membrane. The experiment ended when the hydrogen D-cylinder emptied and could have conceivably continued for many more hours. This membrane was tested for an additional 200 hours under a variety of flow rates and feed pressures prior to the 575 hour test, making the total testing time 775 hours. Further testing is required to establish quantitative lifetimes.

If the properties have been properly engineered, the composite membrane must also show increased performance to that seen by pure palladium. This was tested by comparing a multilayer metal membrane with a thickness of 0.5 µm of palladium on both sides of a 40 µm vanadium foil to a sheet of palladium foil with a thickness of 40 µm. Both membranes were tested at 300°C membrane temperature, 200 sccm feed flow rate, and an identical feed pressure range to produce a fair comparison. The results are shown in Figure 3. From this, it is possible to see that the use of the composite membrane provides far superior performance in terms of the membrane flow rate compared to that of pure palladium. At a pressure differential of just over half an atmosphere, i.e., 20

torr$^{0.5}$, the flow rate per area through the composite membrane was 105 sccm/cm^2 compared with 6 sccm/cm^2 for the palladium foil. Thus, the composite membrane showed an improvement of a factor of almost twenty in the flow rate over the pure palladium membrane. This increase shows that it is indeed possible to increase the hydrogen flow by replacing the bulk palladium that has low transport rates with a material that has much higher transport rates.
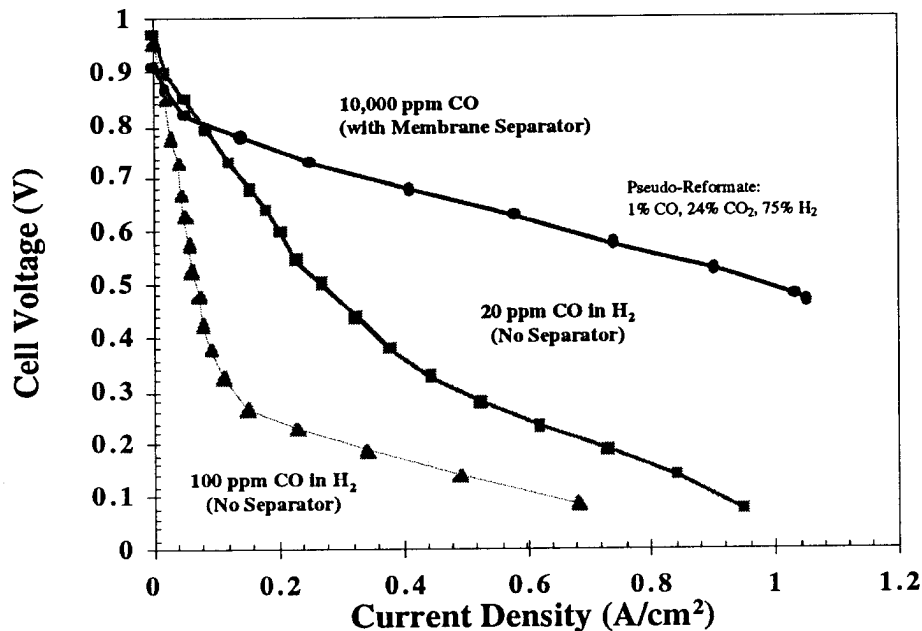

Figure 1. Current-Voltage curves depicting a single cell PEMFC operating at 80°C on (a) pseudo-reformate (1% CO) fed through a hydrogen membrane separator, (b) 20 ppm CO in hydrogen, and (c) 100 ppm CO in hydrogen.
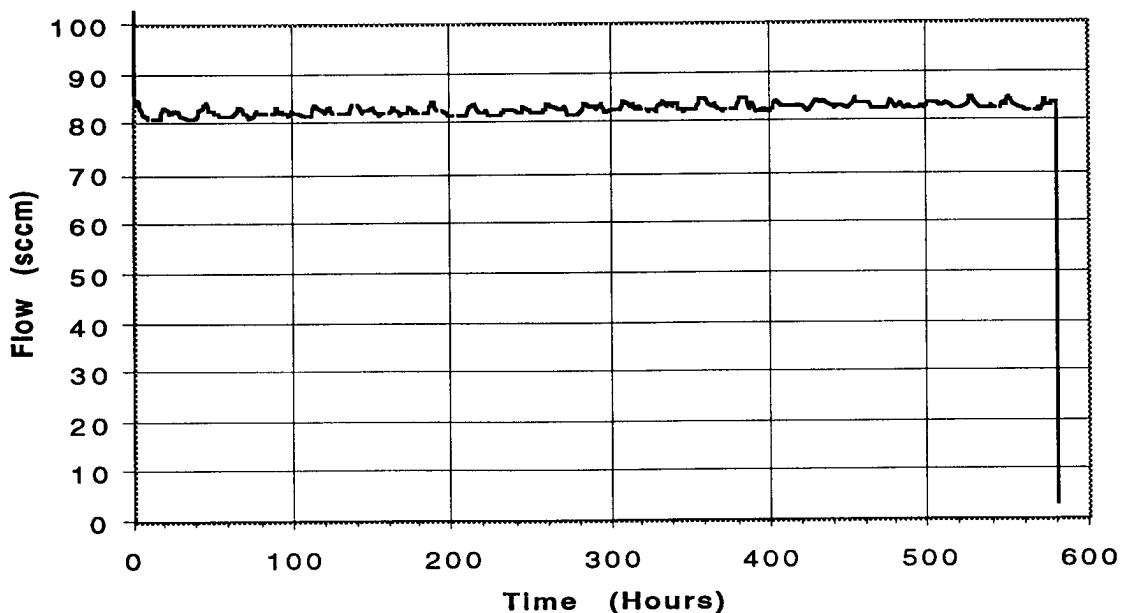

Figure 2. The hydrogen flow is stable at 7.78 sccm per cm^2 membrane and 84% efficiency in this 575 hour test.
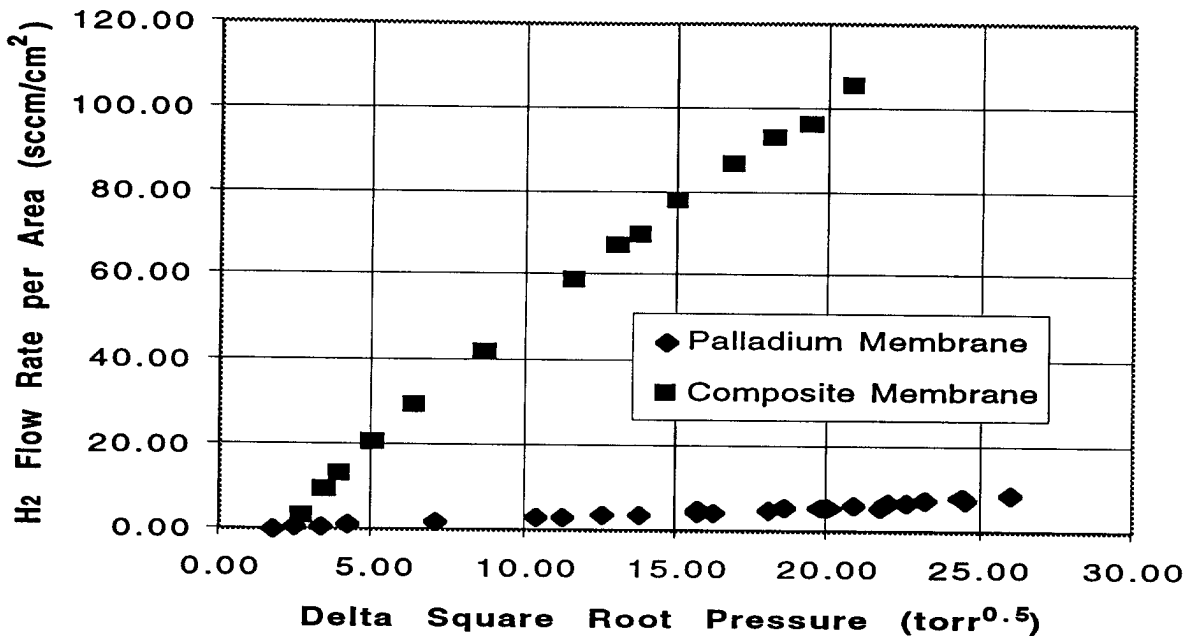
Figure 3. The composite membrane shows an order of magnitude increase in performance over a pure palladium membrane.

Summary

The need for cost effective solutions for hydrogen separation continues to be an area of economic importance. High purity hydrogen use is clearly on the raise due to processing demands. Government is also impacting the increased use of hydrogen by implementing clean air legislation. New membrane solutions can play a key role in advancing hydrogen separations for the up-coming "hydrogen economy". Membranes, such as the one developed at Los Alamos National Laboratory, are a vital step toward improving the products we buy and the air we breathe.

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Report Number (14) LA-UR--97-3968
CONF-9710158--

Publ. Date (11) 199712
Sponsor Code (18) DOE/MA ; DOE/MA; XF
UC Category (19) UC-904; UC-901, DOE/ER

DOE