Hydrogen Purification

H_2

Walt Pyle

Above: Electrolyzers driven by photovoltaics.

Hydrogen gas (H_2) can be used for cooking, water heating, space heating, electricity generation, welding and cutting, and the synthesis and purification of other chemical materials. When hydrogen is made from water and renewable energy resources such as PV, wind, or microhydro, we refer to the produced gas as "solar-hydrogen."

Solar-hydrogen is a sustainable carbon-free gas. It can release heat when burned with air or oxygen, or produce electricity when combined electrochemically with oxygen in a fuel cell. When solar-hydrogen is made or burned, there is no carbon monoxide, carbon dioxide "greenhouse gas," or hydrocarbon pollutants produced.

This article discusses hydrogen purification as a prerequisite to storage or utilization, and covers safety considerations in home power applications.

Where Does Hydrogen Gas Come From?

1. RE Electrolysis of H_2 Gas

We use PV electricity to run an alkaline electrolyzer to produce hydrogen gas. Unfortunately, we do not have a creek or other water resource nearby for micro-hydro electricity production. We could really use it during the rainy season when there is less solar insolation. Since we are located on a hillside in an urban area, a wind generator tower would not be a welcome addition to our neighbors' view. With this in mind, we use PV electricity as the exclusive renewable power source for our hydrogen plant.

Solec 50 peak-Watt PVs *(A, see diagrams on pages 43 and 45)* are arranged in eight panel arrays. They are wired in series-parallel for 24 Volts. Three of these arrays, totaling 24 panels, will produce sufficient power to run our Hydrogen Wind twelve-cell electrolyzer at nearly its rated 1 kW capacity.

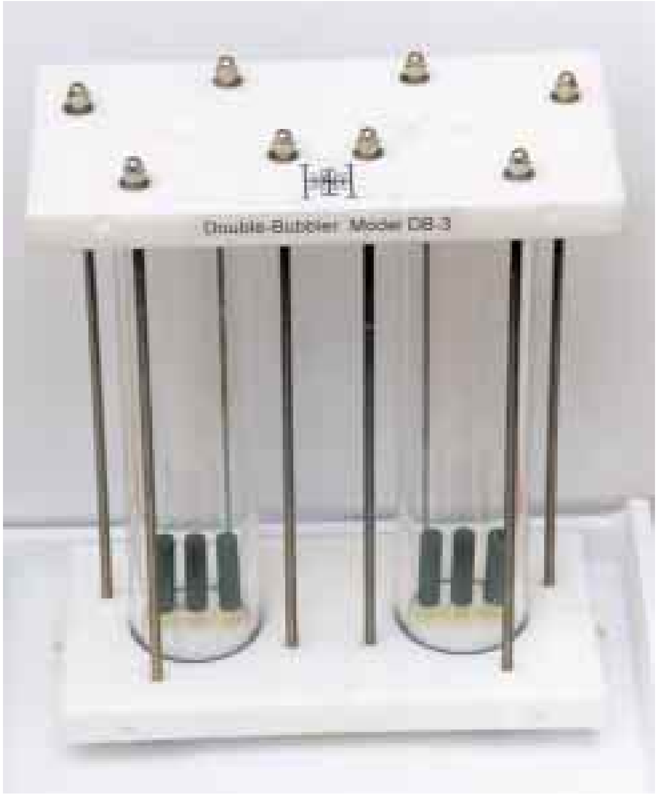
Our Hydrogen Wind electrolyzer *(B)* is shown in the diagrams with its associated purifiers and storage tanks. For more information on the production of hydrogen by electrolysis and hydrogen storage, see *HP39* and *HP59*, respectively.

2. Industrial Cylinder H_2 Gas
We can buy hydrogen gas in high pressure cylinders from a welding supply house. The industrial grade is about 99.5+% pure hydrogen. It may have a few parts per million of hydrocarbons, water vapor, helium, oxygen, and nitrogen contaminants present. These cylinders come in four volumetric sizes, and have 120 to 240 bar (1800 to 3500 psig) pressure ratings. The most common cylinder size is six cubic meters (215 cubic feet). Most industrial hydrogen is made by steam-reforming natural gas.

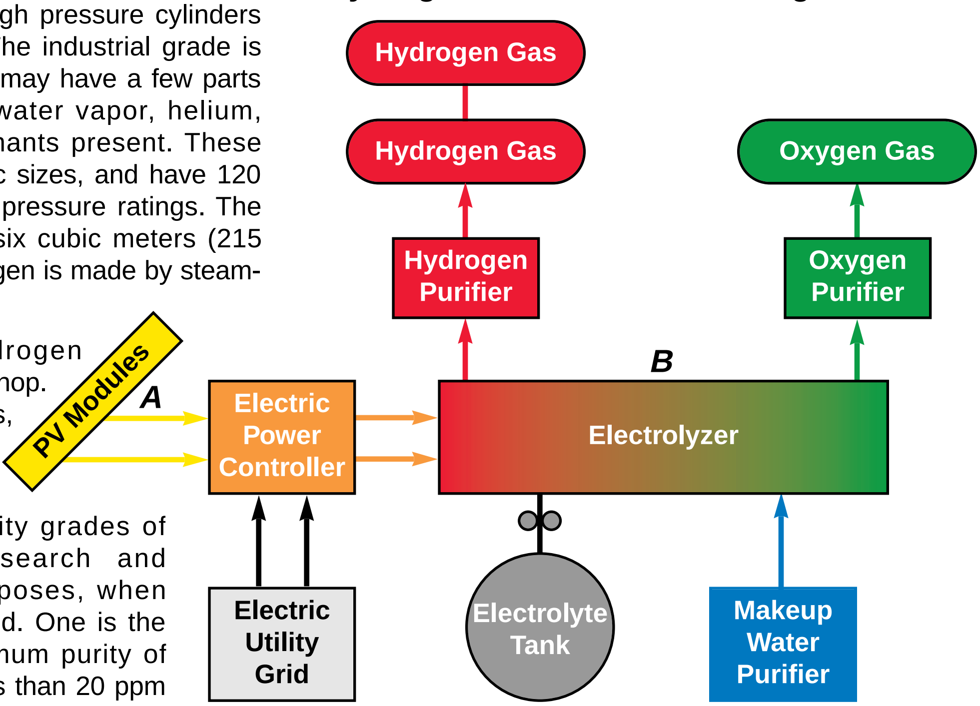
In the past, we bought hydrogen cylinders and used them in our shop. Now that we make our own gas, we rarely have to purchase it.

3. High Purity Industrial H_2
There are several higher purity grades of hydrogen available for research and metallurgical processing purposes, when contaminants must be minimized. One is the "pre-purified grade" with minimum purity of 99.95%. This grade contains less than 20 ppm oxygen with a dew point of less than -59°C (-75°F). This quality of hydrogen is often referred to as "3-nines."

Below: The Double-Bubbler™ removes particulate matter and KOH from the hydrogen gas by passing it through a column of water.



Hydrogen Production Flow Diagram



Another high-purity hydrogen, the "ultra-high purity (Gold Label) grade," provides 99.999% molecular hydrogen. Sometimes this is called "5-nines" purity. For those who demand the best, there is "Research Grade". This grade has even fewer impurities, and is available in small lecture bottles.

4. Cryogenic Liquid H_2
Liquid hydrogen is primarily used as rocket fuel or for large industrial sites. The only significant impurity is helium. We have never used liquid hydrogen for home applications, because special tanks are required. The cryogenic tanks have dual walls. The space between the walls is evacuated and filled with radiation reflective multi-layer insulation. Some experimental cars have been run on liquid hydrogen.

6. Common-duct Hydrogen-Oxygen
Common-duct hydrogen-oxygen welding gas is commonly referred to as either Rhodes' gas or Brown's gas. This gas consists of hydrogen that comes from a "common-duct" electrolyzer, mixed with oxygen. It is VERY dangerous. H_2 + O_2 mixtures should NEVER be stored. Common-duct electrolyzer hydrogen is not suitable for use in hydrogen fuel cells, catalytic heaters, or diffusion burners.

The only sensible application for common-duct hydrogen is to run welding and cutting torches. When it is used in this manner, there is no storage and the gas is consumed as it is made.

Above: The Double-Bubbler™ and purifier system.

What Contaminants May Be Present in H_2?

1. Solid Particulate Contaminants in H_2 Gas

It is possible to find entrained particles of dirt and rust in a hydrogen electrolyzer's product stream. Some electrolyzers have steel or iron alloy containers, valves, and piping. This metal may produce low levels of rust particles over time. Electrolyzers frequently use high surface area electrode materials such as nickel that may lose small particles into the electrolyte. Sometimes, particles of either plastic or sealant will enter the electrolyte system. This happens due to poor housekeeping during manufacturing or repair. These particulates can be removed from your hydrogen gas stream with an appropriate scrubber or filter.

2. Liquid Contaminants in H_2 Gas

Electrolyte is the normal liquid contaminant in an alkaline electrolysis system. In this case, it is water plus potassium hydroxide (KOH). A small amount of KOH and water escapes from the electrolyzer with the flow of hydrogen. An aerosol of fine electrolyte droplets is produced as bubbles of hydrogen gas rise to the surface of the liquid electrolyte and then pop. The same thing happens on the oxygen side of the electrolyzer.

In our Hydrogen Wind electrolyzer, there is another source of KOH/water aerosol hydrogen contamination: electrolyte-wetted float valves that control the discharge of gas from the unit. Any other liquid contaminant in the hydrogen gas would be unexpected. A coalescing filter can remove solids and liquid KOH/water aerosol droplets.

3. Gaseous Contaminants in H_2 Gas

Under certain conditions, we find gaseous contaminants such as oxygen, nitrogen, argon, and water vapor in our hydrogen gas.

Oxygen, nitrogen, and argon are present in normal air. When all three of these gases are present in the normal proportions, an air leak into the electrolyzer or its piping has occurred. However, this is rare. Usually, this is seen only at startup of the electrolyzer when purging or evacuation is imperfect. It also can happen when there are significant leaks in either the cells or in the interconnecting piping. Once the electrolyzer is operating above atmospheric pressure, no outside air will leak inside. However, some hazardous electrolyte may leak out if there are any poor seals. See *HP39* for safety information on handling alkaline electrolyte, as KOH is very corrosive to skin and eyes. Nitrogen and argon are not a safety concern, as they are inert gases. Oxygen is the contaminant of primary concern.

Water vapor is always present in a KOH/water electrolyzer. The gas vapor space of each cell is saturated with water above the electrolyte. The concentration of water saturation is governed by the temperature and pressure in that environment. The objective in a purifier system is to remove excess water vapor. This prevents condensation from occuring downstream, with subsequent flooding of other components. The presence of some water vapor in hydrogen that has been purified for storage in pressure tanks is not harmful—as long as a compressor is not used. The presence of water vapor in stored hydrogen gas slightly reduces its flammable limits in oxygen or air. Our electrolyzer produces gas under pressure, between 0.1 and 4 bar (1 to 58 psig), depending on storage tank pressure.

What are the Methods for Purifying H_2?

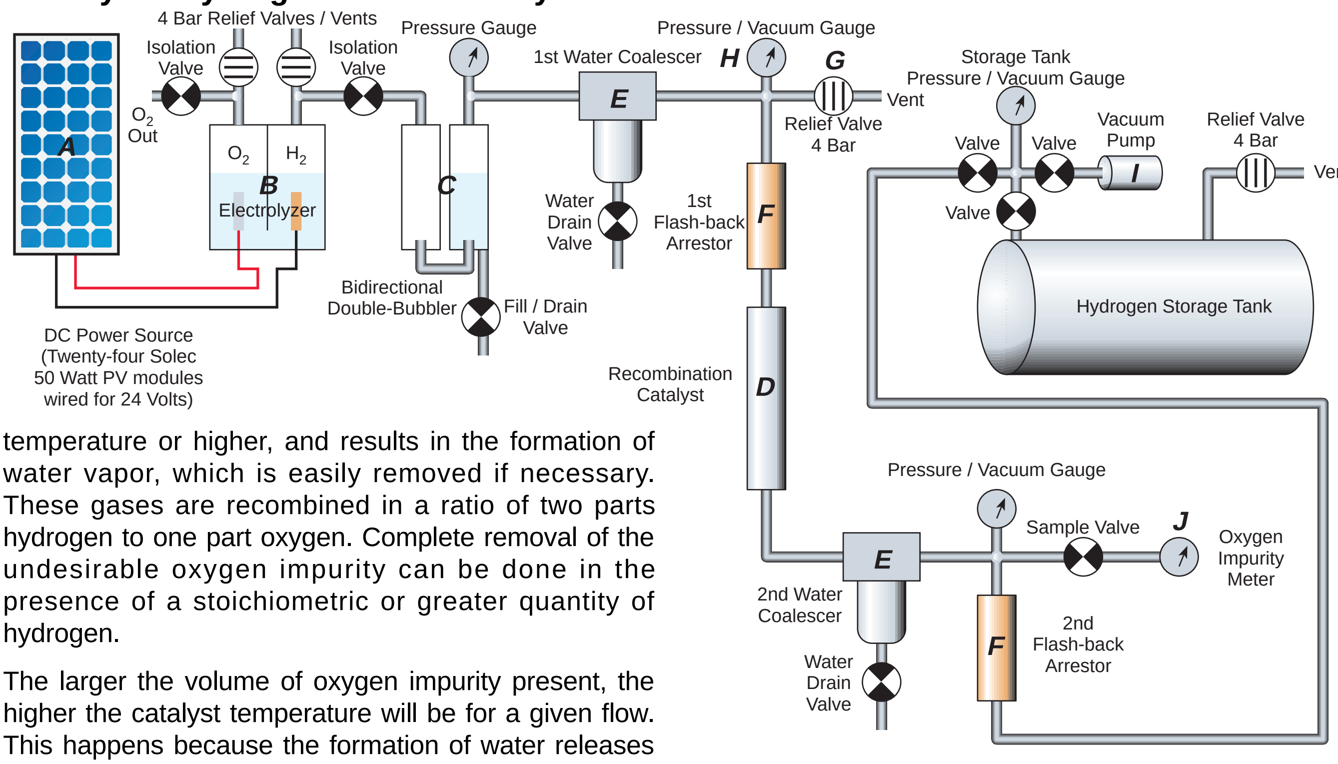
1. Scrubbers for Particulate and KOH Removal

Hydrogen gas that is contaminated by KOH/water electrolyte can be scrubbed by passing it through a water column in a Double-Bubbler™ *(C, see diagram on page 45)* to remove the KOH.

2. Catalytic Recombination Purifier to Remove O_2 Impurity

The catalytic recombination of hydrogen and contaminant oxygen is usually accomplished at room

Walt Pyle's Hydrogen Production System



temperature or higher, and results in the formation of water vapor, which is easily removed if necessary. These gases are recombined in a ratio of two parts hydrogen to one part oxygen. Complete removal of the undesirable oxygen impurity can be done in the presence of a stoichiometric or greater quantity of hydrogen.

The larger the volume of oxygen impurity present, the higher the catalyst temperature will be for a given flow. This happens because the formation of water releases heat.

Usually, the catalysts that are used for removal of the oxygen impurity from hydrogen (or vice versa) are based on platinum group metals (PGM). Thin films of PGM are supported on the surface of alumina pellets. The catalyst pellets are contained by screens in a section of pipe. The hydrogen gas flows through the pipe as it is being treated.

The catalyst will not work while wet. Care should be taken to avoid water condensation on the catalyst. If it becomes wet, simply dry it out before using. Removal of oxygen from hydrogen is called deoxygenation. Our catalytic recombiner *(D)* was designed to be capable of removing up to 3% oxygen from a hydrogen production stream, reducing the oxygen content to less than 1 ppm.

3. Polymeric Hollow-fiber Membrane Purifiers

Polymeric membranes employ the principle of selective permeation to separate gases. Each gas has a characteristic permeation rate. This rate is a function of the ability of a gas to dissolve and diffuse through a membrane. This allows "fast" gases like hydrogen to be separated from "slow" gases like oxygen. Some membrane separators use bundles of tiny hollow fibers inside a containment vessel or pipe.

During the process, a differential pressure develops across the fibers. This pressure drives the flow of the faster gas through the wall of the fiber. In this example, the faster gas is hydrogen. This results in the production of a purified hydrogen stream called the "permeate." To accomplish an efficient separation, the differential pressure must be 8 bar (100 psig) or greater. Monsanto makes this type of purifier for industrial hydrogen recovery under the Prism and Permea trademarks. At this time, they do not offer a purifier small enough to be used in a home-sized hydrogen plant.

4. Palladium-Silver Membrane Purifiers

Ultra-pure hydrogen can be obtained by diffusion through palladium alloys. Palladium is unique: it is extremely permeable to hydrogen, and it can store up to 1000 times its own volume of hydrogen! The mechanism of hydrogen diffusion through palladium alloy has six steps: adsorption, dissociation, ionization, diffusion, reassociation, and desorption. Johnson-Matthey, Inc. and Teledyne Wah-Chang manufacture membranes of this type.

Almost no hydrogen will flow through the membrane at room temperature. Operating conditions required for palladium alloy membranes include temperature of approximately 200 to 800°C (392 to 1472°F) and differential pressure across the membrane of 3 to 12 bar (44 to 180 psig).

In our renewable energy system, we did not have energy to spare for heating the purifier. In addition, our electrolyzer did not produce sufficient pressure to

Above: The relief check valve, pressure/vacuum gauge, and tops of a flash-back arrestor and coalescer.

operate a palladium membrane separator. A solar thermal source could be used to heat a palladium membrane purifier and reopen this option.

This a very attractive method for simultaneously removing water and oxygen from hydrogen. It is also the most expensive hydrogen purification option reviewed. We priced one for our 1 kW hydrogen generation plant and found a small lab-sized palladium-alloy membrane purifier for about $2000. This is the purest hydrogen gas available, 99.999999% purity. Yes, that's "8-nines." Oxygen cannot pass through the membrane, so safety is increased for hydrogen gas storage when these membranes are used for purification.

5. Hydrogen Dryers for Removing Moisture

Water contamination of hydrogen can be reduced by coalescers, refrigeration dryers, membrane dryers, molecular sieve dryers, and desiccant dryers.

Coalescers *(E)* are designed to cause combining of smaller aerosols into larger droplets, susceptible to the effects of gravity. Coalescers remove sub-micron solids and aerosols by three different mechanisms. First, particles in the range from 0.001 to 0.2 microns collide with the filter media and are subject to diffusion coalescing. Second, particles in the range of 0.2 to 2 microns are intercepted by 0.5 micron glass fibers. The efficiency of the interception mechanism increases as the pore size decreases. Third, particles 2 microns and larger are removed by direct inertial impacting, because of their larger mass and momentum. A coalescer is one of the most cost-effective water aerosol removers.

Refrigeration dryers cool the gas and dry it by condensation to a low dew point. These dryers use electric motor compressors and refrigeration fluids in a conventional Joule-Thompson expansion scheme. We did not choose a refrigeration dryer for our solar-hydrogen plant because of energy consumption, cost, and reliability concerns. Perhaps an absorption refrigerator could be applied to this process with solar thermal energy to reopen this option.

Membrane dryers utilize a hygroscopic ion exchange membrane to selectively remove water vapor from mixed gas streams. It can be thought of as a desiccant in tubular form. Tubes are bundled together inside a pipe shell so that the wet feed gas stream flows through the tubes and wets the inside walls. A counter-current dry gas stream flows on the outside of the tubes and purges water from the shell. A disadvantage of this type of dryer is that the dry purge-gas flow rate is greater than the wet product feed rate. Perma Pure Products, Inc. makes this kind of gas dryer.

Another substance used for drying gas is zeolite. Zeolites are alumino-silicate mineral particles that absorb and desorb large quantities of water reversibly. Water absorption on these so-called molecular-sieve dryers is by way of a physical rather than chemical reaction. Zeolite dryers are regenerated thermally in their piping containers by heating them up to 550°C (1000°F) while purging with a dry gas. For continuous operation, two units are used. One is drying gas while the other is regenerating. RSI, Inc. makes small molecular-sieve zeolite dryers for hydrogen. We did not select a zeolite dryer for our solar-hydrogen plant because of concerns about energy consumption for the heat regeneration cycle. A solar heated regenerator would reopen this option.

Right: A flash-back arrestor.

Desiccant dryers absorb water vapor from the gas by contact with a chemical substance like calcium chloride. One popular lab gas desiccant is called Drierite. It includes a color indicator to show when the desiccant must be regenerated. The color turns from blue to pink when water is absorbed. The desiccant is dried by heating or evacuation for recycle.

Safe H_2 Storage

You are responsible for the purity of the solar-hydrogen to be stored. Hydrogen and oxygen mixtures are not safe to store. Make sure that your gas is at least 99% pure hydrogen before storing it in a tank. Measure your hydrogen gas purity with a quality instrument to be sure it is safe.

Oxygen is the impurity of concern, so measure for it in your hydrogen on a regular basis. The strategy for safe hydrogen storage includes using 99+% pure gas, and eliminating the oxygen impurity.

Homebrew Purification System

A hydrogen purifier was constructed for our 1 kW home-scale alkaline-electrolysis hydrogen production plant. We chose a catalytic recombination process to remove the oxygen impurity. Details are shown.

A Double-Bubbler *(C)* with water columns and sparger-frit aquarium-type bubblers can provide several useful functions. It can serve as a visual flow indicator, KOH scrubber, flame arrestor, liquid back-flow preventer (for intermittent operation), upstream or downstream leak detector, and imbalance detector (requires 2 units for comparison of O_2 and H_2 production).

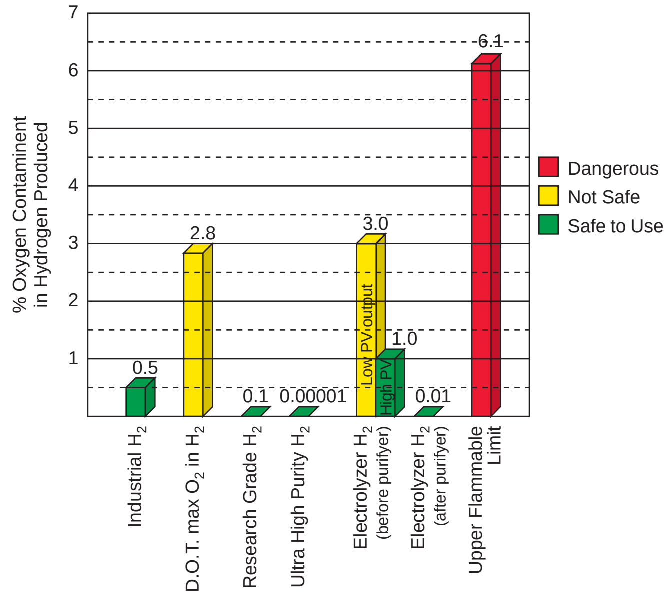
The water in the bubbler columns must be changed during regular maintenance servicing, as it becomes alkaline over time. Some operators have reported using cider vinegar instead of water for longer life between column liquid changes. A color change apparently occurs when the acidity of the vinegar is neutralized by the KOH/water aerosols. Soon, we're going to try it here to see for ourselves.

Water Coalescers and Water Drain Valves

Our coalescers *(E)* have stainless steel bodies, and bowls with replaceable filter elements inside. The coalescer filter removes rust, nickel, plastic, and dirt particles from the hydrogen gas stream. Coalescers also remove water vapor aerosols, known as fog.

The first coalescer removes bubbler aerosol. The second removes recombination-water aerosol, produced by deoxidation of the hydrogen as it passes over the catalyst beads. Our coalescer is a Finite unit manufactured by Parker Hannifin Corp. It captures water aerosols in the 0.001 to 10 micron size, using a glass micro-fiber element. We chose to use a type C

Safety Levels of Oxygen Contamination



filter media in the coalescers. It is compatible with hydrogen gas and can be used on the oxygen side as well.

These coalescers are position-dependent, and must be mounted so that their water capturing bowls and drain valves face down. The coalescers require horizontal piping connections at the entrance and exit. With horizontal piping, the bowls will gravity fill with coalesced water.

Each coalescer is equipped with a small ball valve on the bottom of the bowl to allow regular draining of water captured from the hydrogen. The coalescers must NOT be allowed to fill up with water. We drain the water from the coalescers about once a week.

Flash-back Arrestors

Flash-back arrestors (FBA) *(F)* are used to isolate the purifier from other components upstream or downstream in the hydrogen system piping. An FBA will stop a flame from propagating through a pipe.

Hydrogen is flammable and easily ignited when oxygen is present. The FBA isolates flammable air and hydrogen, or oxygen and hydrogen mixtures, from any source of ignition. An open flame, spark, or hot metal surface can be a source of ignition.

A catalyst can also be a source of ignition, even at room temperature. By bracketing the catalyst with an FBA on either side, the upstream or downstream mixture will not be ignited. This is true even if there is a flammable mixture in the line due to a malfunction or mistake.

FBAs are made with a plug of fine silica sand restrained by screens in a wide section of piping. The sand

Left: The Panametrics XMO2 oxygen analyzer measures the amount of O_2 contaminant in the hydrogen.

quenches any flame-front and stops combustion. We prefer the FBAs that have an integral check valve to prevent backflow. Western Enterprises, Inc. makes an FBA appropriate for hydrogen and acetylene gas service.

Check Valve Pressure Relief
A check valve *(G)* for pressure relief is set to 4 bar (58 psig) to prevent over-pressuring the system by error. If this pressure is exceeded, the relief check valve "cracks" and hydrogen gas is released out of the vent line. When the pressure is reduced to the normal operating value (0.5 to 3.5 bar gauge), the valve closes once again. Relief valves are subject to drift over time, so check to be sure that the set pressure and the actual pressure are the same. This should be done at regular maintenance shutdowns.

Compound Pressure Gauges
We use pressure gauges *(H)* with all stainless parts to prevent corrosion failure. They are compound gauges measuring both vacuum and pressure. We use the vacuum gauge function to evacuate the system after maintenance, or before startup of the hydrogen plant. The pressure gauge monitors operation of the plant when making hydrogen gas.

De-oxo Catalytic Recombiner
Our catalyst *(D)* is packed in a stainless steel tube by the supplier and performs the key purification function: removing oxygen from the hydrogen gas stream. The catalyst tube must be placed so that the flow enters through the top and exits at the bottom. This will prevent lofting the particles in the catalyst bed and fluidizing them. Keeping the catalyst pipe vertically oriented helps to keep the flow uniform. Thus, the water formed during de-oxo purification flows towards the bottom in the same direction as the hydrogen gas. It can be removed from the purified hydrogen by the second coalescer before it reaches the second FBA.

Connecting the Purifier to the Electrolyzer
The hydrogen duct coming from the electrolyzer is first connected to the gas inlet port of the Double-Bubbler for KOH/water scrubbing. The scrubbed hydrogen gas is then fed to the purifier for oxygen removal. We used 1/4 inch stainless tubing with Swagelok fittings to connect the electrolyzer, bubbler, and purifier.

Purging the Purifier
Before starting the hydrogen plant, flush any possible flammable gas mixture out of the piping with an inert purge gas, like nitrogen or carbon dioxide.

An alternate method to remove flammable gas mixtures from the piping and other components is to use a mechanical vacuum pump *(I)*. It must be capable of producing a vacuum of at least 20 mbar (approximately 20 Torr). A vacuum cleaner will not work for this. A two-stage laboratory vane-type vacuum pump with a thermocouple pressure gauge will work well.

Compound pressure gauges are very useful, because you can see when the vacuum has reached less than 20 millibar (>29 inches Hg vacuum). It is also easy to check if the piping holds vacuum after the pump is removed. Vacuum measurement units have become more standardized in recent years. Unfortunately, many gauges are still on the market that register vacuum in inches or millimeters of Hg (mercury) below atmospheric pressure. This can be confusing to the uninitiated.

Startup of Electrolyzer and Purifier
Once the purifier is ready, we start the electrolyzer by closing the main electrical breaker to the DC power supply. Then, we wait twenty minutes or so for the float valves on the Hydrogen Wind electrolyzer to fill. Next, we close the vent valve on the electrolyzer. Pressure in the electrolyzer will begin to rise. Slowly, we open the isolation valve between the electrolyzer and the Double-Bubbler. Gas will enter the purged purifier. After the hydrogen flow through the Double-Bubbler has stabilized, we open the isolation valve all the way, and leave the valve open.

Measuring Hydrogen Purity
When production of gas is underway, we check the purity of the gas before storage. Several oxygen meters are available. We use a Panametrics XMO_2 oxygen

analyzer (*J*) that has a range of 0 to 5% oxygen. This meter has high accuracy and is reliable. A less expensive oxygen meter is available from Figaro USA. Our hydrogen has less than 0.01% oxygen after the purifier. We have used this catalytic purification system continuously for almost three years with no loss in performance.

Future Direction

We are now planning to store and use the electrolyzer's purified oxygen production for both fuel cells and a hydrogen-oxygen torch. The purifier has been operational for almost a year. Since we lack a suitable meter to measure the hydrogen contaminant in the oxygen, we still vent it to the atmosphere. Next month, our long-awaited hydrogen meter from DCH, Inc. is due to be delivered. The DCH meter is designed to measure from the ppm level to 100% hydrogen. In a future article, we will share our experience with oxygen purification and storage.

Acknowledgements

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Access:

Author: Walt Pyle, H-Ion Solar, 6095 Monterey Ave., Richmond, CA 94805 • 510-237-7877
Fax: 510-232-5251 • hionsolar@aol.com
Web: www.hionsolar.com

Safety Information:
Air Products and Chemicals, Inc., "Safetygram 4" on Gaseous Hydrogen • 610-481-4911

Alkaline Electrolyzer:
Hydrogen Wind Inc., RR2 Box 262, Lineville, IA 50147
515-876-5665

Catalyst Suppliers:
Resource Systems Inc., Six Merry Lane, East Hanover, NJ 07936 • 973-884-0650 • Fax: 973-515-3166

GPT, Inc. • 732-446-2400 • Fax: 732-446-2402

Coalescer:
A.F. Equipment Co., Inc., 1273 Forgewood Ave., Sunnyvale, CA 94089-2216 • 408-734-2525

Parker Hannifin Corp., 17325 Euclid Ave., Cleveland, OH 44112 • 800-506-4261 • 216-531-3000

Complete Purifier System (Model PT-4) and Double-Bubbler (Model DB-3):
H-Ion Solar, Inc., see Walt Pyle above.

Flash-back Arrestor
(Western Enterprises Model FCV-3A):
Atlas Welding Co., 1224 6th Street, Berkeley, CA 94710
510-524-5117 • Fax: 510-524-9098

Hydrogen Membrane Dryer:
Perma Pure Products, Inc. • 732-244-8140

Palladium-alloy Membrane:
Johnson Matthey, Inc. • 44-1763-253306 (Great Britain)
610-971-3100 (USA)

Teledyne-Wah Chang, Inc. • 541-967-6904

Polymeric Membrane:
Permea, Inc. • 800-635-8842

Pressure Gauge:
Fluid Gauge Co., P.O. Box 881833 San Francisco, CA 94188 • 415-285-0648

Stainless Pipe Fittings:
Oakland Valve and Fitting Co., 2441 Sprig Ct. - Unit A, Concord, CA 94520• 510-676-4100
Fax: 510-798-9833