Solar Hydrogen Production by Electrolysis

Walt Pyle, Jim Healy, Reynaldo Cortez

Why would anyone want to produce hydrogen at home? Hydrogen can be used as a non-toxic energy storage and transport medium. Hydrogen that is made from water using solar energy is a sustainable and renewable home energy supply. Make hay (or hydrogen) while the sun shines. Then use the stored hydrogen to produce heat and electricity on demand, day or night!

We got excited about solar hydrogen production during the seventies and the first oil shocks. What happened between the seventies and nineties? For the most part we worked with thermolysis (splitting water with concentrated solar heat) and photoelectrolysis (splitting water in a liquid solar cell). We also followed the work of other hydrogen pioneers, such as Roger Billings and his associates, who produced and used hydrogen in home appliances and vehicles.

The article by Richard Perez about the Schatz PV Hydrogen Project (*HP* #22, pp. 26–30) and a subsequent visit to Humboldt State University's Trinidad Marine Laboratory launched us into designing and making a "home-sized" system based on electrolysis of water. Electrolysis is the competition for thermolysis and photoelectrolysis at this juncture.

Hydrogen and oxygen can be produced from water using electricity with an electrolyzer. This article describes the installation and operation of a 12 cell Hydrogen Wind Inc. 1000 Watt electrolyzer. This electrolyzer can produce 170 liters/hour (6 cubic feet/hour) of hydrogen and 85 liters/hour (3 cubic feet/hour) of oxygen (at standard temperature and pressure).

In addition, we describe a homebrew purification and storage system for the hydrogen and oxygen produced by the electrolyzer. With proper after-treatment, the gases produced can be stored safely. The purified hydrogen and oxygen can be used in fuel cells (to produce direct current electricity) and catalytic burners (for heating and cooking) without poisoning or damaging the noble metal catalyst materials. The gases can also be used for welding and cutting, as well as for motor vehicle fuel.

!!!!Safety First!!!!

Making and storing hydrogen and oxygen is not kid's stuff — this is "rocket fuel"! Use flashback flame arrestors on the hydrogen and oxygen outlets from the electrolyzer. Secure dangerous caustic from small prying hands. Make sure your gases are pure before storing them. More on safety follows.

How Much Hydrogen Do I Need?

This varies tremendously from household to household, depending on how well the Demand Side Management job has been done. We can run our Platinum Cat space heater for about three hours on a cubic meter of hydrogen. The amount of gas needed can be estimated from the energy consumption of any appliance. Amanda Potter and Mark Newell's article in *HP* #32 (pp. 42–45) describes the operation of an electrolyzer and shows how to calculate the amount of gas needed to run appliances. See articles on hydrogen space heating in *HP* #34, hydrogen cooking in *HP* #33, and making electricity from hydrogen with a fuel cell in *HP* #35.

How Much Power Does It Take?

A cubic meter (35.3 cubic feet) of hydrogen gas takes about 5.9 hours to produce in this electrolyzer, when operated at its rated input power of 1000 Watts. This means the energy required to produce a cubic meter of hydrogen and 0.5 cubic meter of oxygen is about 5.9 kW-hr. This translates to an efficiency of 51%, where 3 kW-hr/m^3 equals 100% efficiency at 20°C. Typical industrial scale plants operate at about 4.5 kW-hr/m^3 or 67% efficiency at high current density. The efficiency is better at lower current density.

What Is Needed to Produce Hydrogen at Home?

Our system includes the following components and sub-systems (see the block diagram next page):

- Solar electric power and/or utility grid power
- Power Controller
- Electrolyzer
- Hydrogen Purifier
- Oxygen Purifier
- Hydrogen and Oxygen Storage Tanks
- Electrolyte Storage Tank and Transfer Pump
- Makeup-water Purifier

Where Can I Get An Electrolyzer?

The Hydrogen Wind electrolyzer was introduced by its designer Lawrence Spicer in *HP* #22 (pp. 32–34). Hydrogen Wind Inc. electrolyzers are available in single cell units for small demand or educational use, and in multiple cell configurations which provide higher gas production rates.

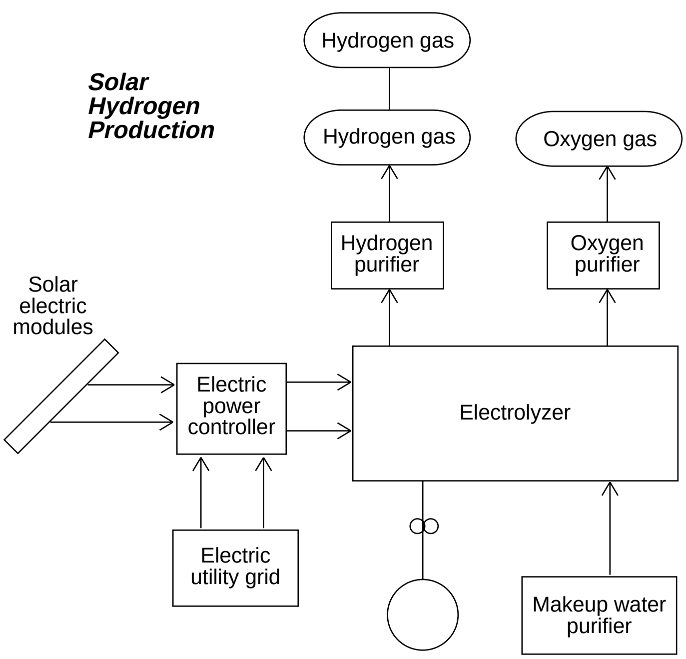
We purchased a 12 cell 1000 Watt system with the gas pressure controls and electrical metering. Larger systems with up to 24 cells or smaller three cell and six cell systems are available. Another article by Spicer, describing the individual cells in more detail along with an introduction to cell arrays, appears in *HP* #26 (pp. 34–35).

The cell electrodes are fabricated from rectangular metal plates with tabs on one end. Both the anode and the cathode metal plates are made from porous, sintered nickel. Two clusters of nickel electrode plates, 14 for the anode and 14 for the cathode, are separated by porous plastic sheets folded accordion style within a separator container.

Above: An overview of the electrolyzer system. The power supplies and electrical controls are on the far left. Purification equipment is to the right of the power controls. The electrolyte reservoir and hydrogen and oxygen float valves with pressure gauges are to the right of the purification equipment. Twelve electrolyzer cells are shown on the far right. A feedwater purification system is just below the twelve electrolyzer cells. The caustic electrolyte storage tank is on the ground below the float valves.
Photo by Reynaldo Cortez

The plastic separator container is open at the horizontal ends, and closed at the top and bottom. This lets the larger hydrogen gas bubbles (which escape from the negative electrode or cathode) rise in the electrolyte, due to their buoyancy, and exit the separator container on one side. The hydrogen remains separate from the smaller oxygen bubbles which evolve from the positive electrode (anode) and exit on the opposite side.

Solar Hydrogen Production



The micro-porous polypropylene separator container and the electrode clusters are housed inside sections of steel pipe with flat steel plates welded on one end and bolted on the other end. The steel cell housings hold the water and potassium hydroxide electrolyte, and keep the hydrogen and oxygen gases apart after they rise from each end of the separator container.

We installed our electrolyzer inside a small weather-protected shelter made from box tubing and sheet metal. We chose stainless steel sheet metal for its corrosion resistance to caustic electrolyte and long-lasting “perma-culture” value. The photograph above shows an overview of the system.

Solar Power and Utility Grid Backup Power

Our solar electric power is produced by two 16-panel Carrizo Solar “Mud” photovoltaic arrays and a gaggle of other smaller panels. On a good summer day we get up to 75 Amperes at 14 Volts for charging the

Above: The bi-directional bubblers and purification systems. Photo by Reynaldo Cortez

house batteries. When the two house battery banks are fully charged, our two 50 Amp SCI charge controllers disconnect the PV power, and the PV voltage rises. An Enermaxer controller senses the voltage rise and transfers the PV power to the electrolyzers to make hydrogen and oxygen during the remainder of the day. A utility grid electrolyzer power supply is used to make hydrogen and oxygen when there is insufficient solar power available.

How Do We Purify the Gases?

The gas purification system is shown in more detail in the diagram on right. The hydrogen gas and the oxygen gas are purified by two different systems.

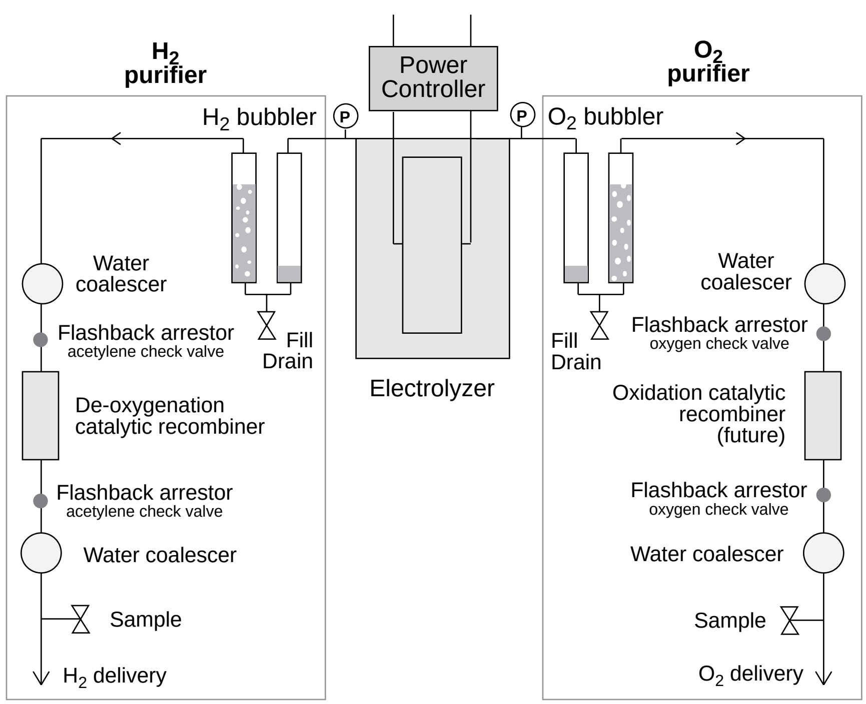
Bubblers

First, each gas is scrubbed by passing it through a water bubbler column. Each of the gas scrubbing bubblers is made from two vertical plastic tubes with end caps. A pair of fish-aquarium type bubbler frits was glued into holes drilled in the inside bottom caps of each acrylic plastic tube, using methylene chloride solvent. Flow of gas into or out of a bubbler can then be seen by the operator. The bubblers are filled about one-third full with distilled water using the drain and fill valves on the bottoms.

We call these “Bi-directional Bubblers”. The bubblers are tolerant of flow in any direction, without letting the scrub-water into the product storage system or the electrolyzer. We got the idea for making these bubblers from Dr. Peter Lehman and his associates at Humboldt State University (Schatz Solar Hydrogen and Fuel Cell Laboratory.)

The gases entering the purifier are saturated with water vapor and may contain minute amounts of caustic electrolyte aerosol and particulates like rust. After passing through the bubblers the gases are still saturated with water vapor, but virtually caustic- and particulate-free. Installing another coalescer before the bubbler would prevent particulates and some aerosol from entering the bubblers.

Gas Purification System



Coalescers
Next, the gases are partially dried by passing them through coalescing filters. Special materials were required for the oxygen coalescer filter to prevent spontaneous combustion, and no oil or hydrocarbons can be present.

Recombiners
The hydrogen gas purifier treats the hydrogen gas in a catalytic recombiner. The purpose of the recombiner is to recombine any oxygen impurity in the hydrogen product, and make water. The noble metal catalytic recombiner removes the oxygen impurity to make the hydrogen gas safe to store and handle. As a safety measure, we installed flashback arrestors between the first and second coalescers and the recombiners. The flashback arrestors prevent flashback of poor purity gases (oxygen impurity in the hydrogen produced) when they reach the recombiner and ignition source. The recombiners must be installed with their major axis vertical and the entry at the top.

Some data recently published by W. Hug et al from the German Aerospace Research Establishment *(International Journal of Hydrogen Energy*, Vol. 18 No. 12, pp. 973–977) shows that purity of the gases produced by an alkaline electrolyzer is affected by the current density and temperature of the cells. From the graphs we see that the purities of the hydrogen and oxygen gases are poorer at low current densities (such as when a cloud covers the sun for example). This is because diffusion of the gases through the liquid electrolyte is a more significant fraction of the total production at low current densities.

The data also imply that there is more danger of having hydrogen impurity in the oxygen than the reverse. Note that the lower flammable limit, 4% for hydrogen impurity in bulk oxygen, is approached at low current densities.

How Does One Store the Gases?
The hydrogen will be stored in two 0.47 cubic meter (125 gallon) propane tanks, and the oxygen will be stored in one propane tank.

REMEMBER: hydrogen gas is safe to store — hydrogen/air or hydrogen/oxygen mixtures are NOT safe to store! Put safety first! Safety is your responsibility. It is our intention to give you the information you need to follow safe practices.

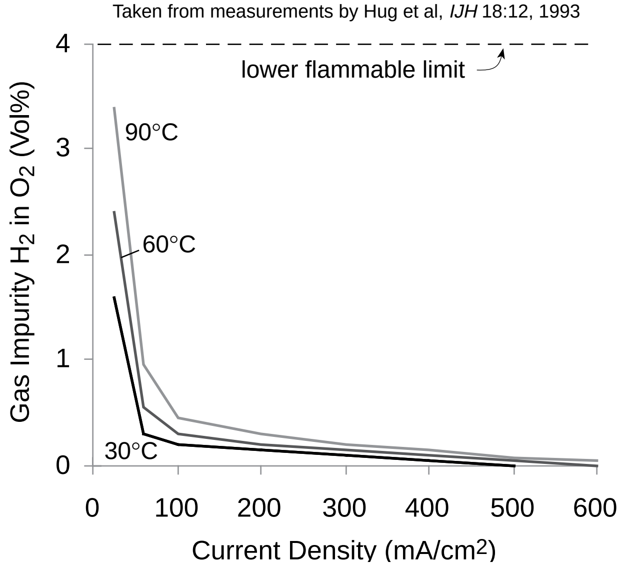
Each of our used propane tanks was cleaned thoroughly and hydrostatically tested to 13.8 bar (200 psig.). Pressure relief valves on each tank are set for 10.3 bar (150 psig.). A pressure switch is installed on the hydrogen tank feed line to shut off the electrolyzer power supply when the pressure reaches 6.9 bar (100 psig.), the rated maximum output pressure of the electrolyzer.

The produced hydrogen gas is pressurized by the electrolyzer to its maximum rated pressure of 6.9 bar or less. Our two hydrogen tanks hold the equivalent of: 6.9 bar x 2 tanks x 0.47 cubic meter = 6.5 cubic meters (at standard temperature and 6.9 bar pressure).

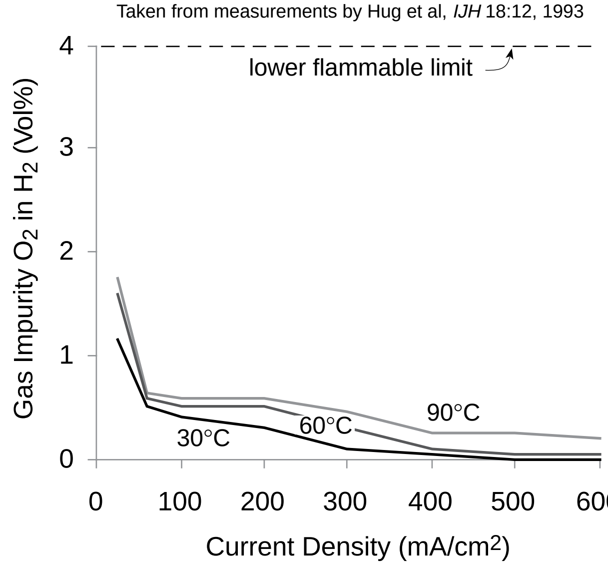
Makeup-water Treatment System
As hydrogen and oxygen are produced in the electrolyzer, water is consumed and it must be replaced. We produce our makeup-water using the local Utility District water, which is piped into the home.

We want to prevent the formation of "mineral scale" on the surface of the electrodes inside the electrolyzer because we want them to last a long time. First, the

Amount of Hydrogen in Oxygen
Taken from measurements by Hug et al, *IJH* 18:12, 1993



Amount of Oxygen in Hydrogen
Taken from measurements by Hug et al, *IJH* 18:12, 1993



Water Purification Results

Element	*Before Purifier, ppm*	*After Purifier, ppm*
barium	0.009	nil
calcium	7.3	0.006
potassium	0.37	nil
magnesium	0.7	nil
sodium	1.8	nil
silicon	3.8	3.8

water is passed through a 20 micron interference filter to remove particulates like rust and sand. Second, the water passes through a charcoal drinking water filter to remove organics and chlorine. Third, the water passes through a de-ionizing column to remove metallic ions. The water before and after the purifier was analyzed. The results are shown in the table above.

As you can see, we removed some scale-forming material. Other elements were below the lower detectable level of the instrument (approximately one ppb). Our water before the deionizer and charcoal filter is not very "hard" at this location; it does not contain very many dissolved minerals. After the de-ionizer there is a marked reduction in elemental concentrations of everything except silicon.

Why Conduct a Hydrostatic Test on the Electrolyzer?
Prior to filling the electrolyzer with caustic electrolyte, we conducted a hydrostatic leak test by filling the cells with purified water and pressurizing the cells and electrolyte reservoir to 6.9 bar (100 psig) using utility line pressure. Several tubing fittings leaked until tightened. Fixing water leaks during the initial hydrostatic test is much better than fixing leaks when they involve caustic electrolyte! Getting caustic on your tools, gloves, safety glasses, and clothes is a real drag. Plan ahead!

When installing the tubing clamps, position them so you can tighten them later when the cells are tied together. An improvement would be to mount the cells higher to allow for access to the clamps from below.

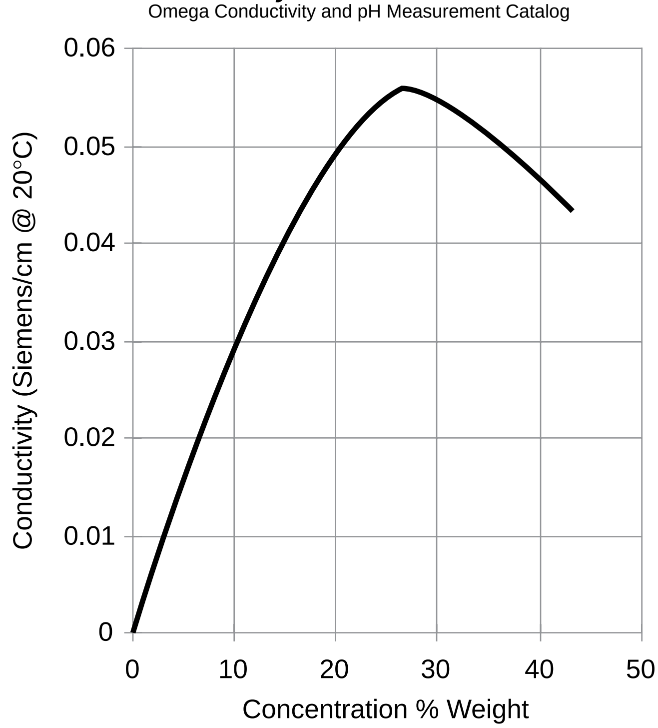
Why Do You Need the Caustic Electrolyte?
Potassium hydroxide (KOH) in the water makes it electrically conductive, so that ions can be transported through the electrolyte during electrolysis. See graph showing the conductivity of the KOH electrolyte as a function of weight percent KOH in water on right.

We have chosen KOH as the caustic. The twelve electrolysis cells and the electrolyte reservoir hold about 61 liters (16 gallons) of water plus 15 kilograms (33 pounds) of KOH. This solution is about 23% KOH by weight. The strength of the electrolyte solution can be tested with a battery hydrometer. The specific gravity should be about 1.1.

Safety is a Must When Handling Caustic Electrolyte!
DANGER!! Potassium hydroxide is very corrosive and hazardous to handle. KOH deserves great respect. Goggles or safety glasses with side protectors, and plastic or rubber gloves are absolutely necessary when handling KOH. When caustic comes into contact with the skin, the natural oils of the skin are chemically converted to a soap, which initially gives a slippery feeling. Prolonged contact will dissolve the skin and give a chemical burn similar but more severe than that given by handling lime or fresh wet concrete with bare hands. The best treatment for any accidental spill is flushing with copious amounts of water, or neutralization with a weak acid such as vinegar. Always have a water hose hooked up and operational before handling KOH caustic. Keep the electrolyzer outdoors and locked so only qualified people can service it. A cyclone fence with top and sides might be the solution.

DANGER!! The mucous membranes of the eye are especially susceptible to caustic damage. It has been estimated that 15 seconds of contact to the eye with concentrated KOH caustic is enough to produce permanent blindness. If any KOH comes into contact with the eyes, the best treatment is to flush the eyes immediately with pure water for at least 15 minutes and seek medical attention.

Conductivity vs. KOH Concentration
Omega Conductivity and pH Measurement Catalog



What Provisions Need to be Considered When Handling Caustic?
To service any of the cells, we need a way to drain the electrolyte and store it for re-use. We have a drain valve and line on the bottom of the electrolyte reservoir that allows the KOH solution to gravity drop into a stainless steel tank at a lower level on the ground. A tubing roller pump is used to refill the electrolyzer cells with KOH after the maintenance is completed. Our KOH tank was previously used as a swimming pool filter case.

We mixed the water and KOH in the ground level caustic storage tank. Water and KOH mixing produces chemical heat, the “heat of solution”, which is surprisingly high. After we mixed in all of the KOH flakes, the water temperature rose from 20°C (68°F) to about 82°C (180°F).

At this point we made our first big mistake. After the KOH and water electrolyte solution was mixed (and hot), we immediately started pumping it into the electrolyzer reservoir and cells, using the tubing pump. Within minutes, the tubing pump began leaking. We stopped the pump and drained the KOH back to the ground level tank. After cleaning up the mess, we found that the silicone tubing had split open. We let the KOH solution cool overnight. The next day we replaced the tubing in the pump, and tried again. This time the transfer proceeded without pump tubing problems.

By the time the caustic was about half pumped into the cells, we found that six of the tubing fittings on the first two cells were dripping KOH onto the floor of the shelter. The hot KOH the night before had damaged some of the pipe thread seals which were made with five minute epoxy. The threads in cells further away from the caustic KOH entry point were not damaged, presumably because the caustic KOH solution had cooled by the time it reached those points. We drained the caustic KOH back to the ground storage tank, removed the affected fittings and replaced the epoxy thread sealant. The next day we filled the cells back up with KOH solution for the third try.

More caustic KOH leaks! This time we had leaks on the tubing fittings on the gas-trap tubing loops where the hydrogen and oxygen come out of the cells at the top. Additional tightening of the tubing clamps with a 12 point box wrench stopped some leaks. Other fittings had to be removed and thread epoxy had to be reapplied. When will solid polymer electrolyte electrolyzer cells be available at a reasonable price so we won’t have to hassle with KOH???

What Were the Cell Operating Conditions?
The cells require about 1.7 volts each to begin operating; at higher currents there is a greater voltage requirement. The direct current requirement is about 40 Amperes for each cell at rated gas output. In a twelve-cell system the cells are wired in series, so that all of the cells get the same current and the voltages add up to 12 x 1.7 V or 20.4 Volts total at 20 Amperes of current. The cells can also be wired in series-parallel for 10.2 Volts total.

Our solar photovoltaic system and grid back-up power supplies can only produce about 25 Amperes at the moment, so we cannot yet achieve full gas output. The 20.4 Volt operating voltage was not a problem with our Carrizo solar electric arrays, however, since they have an open circuit voltage of about 25 Volts.

Strange and Unusual Behavior?
When operating the electrolyzer the first day on direct current power, the power controller behaved predictably. We measured about 22 Volts and 25 Amperes flowing into the electrolyzer cells. We had gas flow only through the oxygen bubbler however!! And occasionally, the oxygen float valve “burped” some KOH solution upward with a release of gas. The fix for this problem was to raise the electrolyte level from about 5 cm (2 inch) on the reservoir level gauge to 20 cm (8 inch).

At first startup the gas comes out after a delay of about an hour while the cells are “charging” and the gas bubbles on the electrodes get large enough to break away. Voltage across the cell array gradually rises during “charging” from 18 to 19 to 20 Volts before gas comes out.

On restart, hydrogen comes out later than oxygen since it must first fill the top of the electrolyte reservoir tank to pressure-pump the system. When both gases were coming out of the electrolyzer pressure control float valves, the pressure on the reservoir was 2.5 bar (36 psig) when discharging to atmospheric pressure.

The next day we may have had our first personal demonstration of William Grove’s astonishing observation that an electrolyzer can run backwards and become a power source. Grove discovered in the early 19th century that the reverse reaction — supplying oxygen and hydrogen to electrodes — causes an electrolyzer to produce direct current electricity and act as a fuel cell.

Before we turned on our power supply the next day, the voltmeter showed about 16 Volts DC on the electrolyzer terminals indicating it was acting as a “source”. After that we put a resistive load on the electrolyzer leads and generated about 16 Volts and 10 Amps for several hours (160 Watts) before it “ran out of gas”. Was the cell acting as a fuel cell, as an alkaline nickel-iron battery, or a combination of both?

Grunting and Wheezing Sounds are Normal!
Inside the Hydrogen Wind gas pressure control system there are three float control valves. Two float valves are used for the oxygen and one is used for the hydrogen. When the float valves are filled with gas (vertical acrylic tubes with top caps), they float on the electrolyte in the chambers. As each chamber fills with gas the electrolyte is gradually displaced and the the buoyancy of the float decreases. When the buoyancy is low enough, the float falls which releases the elastomer plug from the exit passage and allows the gas to leave the system.

The float valves cycle over and over again to release “bursts” of gas to the purifiers. You can hear grunting and wheezing sounds when standing alongside the unit. A little back pressure on the discharge lines makes the release less violent and quieter. With 1 bar (14.5 psig) back pressure we had good results.

Budget & Economics for Gas Production & Storage
The approximate cost for the solar hydrogen system equipment is listed below, broken down by sub-system.

The labor used for this installation was our own and was not tallied. Normally, for a “first time” system such as this, a rule of thumb is that the labor costs will about equal the capital equipment costs. Labor on any future clone would be significantly less. Capital equipment costs could have been reduced by using fewer stainless steel and more plastic components.

We didn’t work out the “payout” or ROCE for this system before going for it. We made it because we thought it was nifty stuff!

It would probably take quite a while to pay for this system. However, don’t forget, it’s a prototype. Mass production has a way of cutting costs by factors of ten. How does a cloned system capital cost of $678 sound?

Status and Future Direction
Startup of this system occurred during the first week of December 1993. Our next task is to measure the purity of the hydrogen and oxygen product gas streams before we attempt storage.

Eventually, when we have a use for the oxygen gas product in a large fuel cell, we plan to add an oxidation recombiner to the oxygen side. This will remove any hydrogen impurity from the oxygen side and make it safe to store and handle. For now, we are not storing the oxygen. Instead, we will supply the oxygen to the root system of vegetables in some experiments with a horticultural friend of ours, but that’s another story......

A future article will focus on safe storage of hydrogen and oxygen. We plan to cover compressed hydrogen and oxygen gas storage and hydrogen storage in metal hydride.

Hydrogen System Cost

Equipment	*Cost*	*%*
12 cell electrolyzer system (incl S&H)	$2,300	34%
Photovoltaic modules (used)	$1,500	22%
Gas storage tanks, relief valves, tubing	$1,100	16%
Hydrogen purification system	$950	14%
Oxygen purification system	$350	5%
Caustic storage and transfer	$300	4%
Feedwater purification system	$275	4%
Total	$6,775	

Acknowledgements
Alternative Energy Engineering, David Booth and David Katz, for the upgrade to our Enermaxer power controller.

Jim Robbers and Mike Robbers for the used stainless steel swimming pool filter cases which we use for electrolyte storage.

Access
Walt Pyle, WA6DUR, Richmond, CA • 510-237-7877

Jim Healy, WH6LZ, Richmond, CA • 510-236-6745

Reynaldo Cortez, Richmond, CA • 510-237-9748

Electrolyzer
Hydrogen Wind Inc. RR 2 Box 262, Lineville, IA 50147 • 515-876-5665

Purifier and Storage Components
Hydrogen Coalescer (Coilhose 27C3-S): Weill Industrial Supply Inc. • FAX 510-235-2405

Bi-directional Bubbler: H-Ion Solar Co. • FAX 510-232-5251

Flame Arrestors: Check valve flashback arrestor, flash arrestor body with female inlet check valve. Part # FA-3CV. Western Enterprises • FAX 216-835-8283

Oxygen Coalescer Finite Housing S2M-2C10-025: A F Equipment Co. • 408-734-2525

Hydrogen Recombiner Deoxo Purifier D50-1000: GPT Inc. • FAX 908-446-2402

Pressure Relief Valves (Nupro 177-R3A-K1-A): Oakland Valve & Fitting Co. • FAX 510-798-9833

Power Sources
Solar arrays: Carrizo Solar Corp. • 800-776-6718

Enermaxer controller: Alternative Energy Engineering (see ad index) • 800-777-6609