An Extended Time Operational Study of a Hydrogen Electricity Generator Based Off a Modification of the Linnard Griffin Electrolysis Patent.

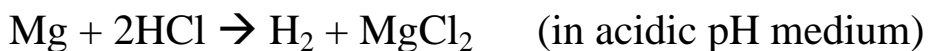**David B. Rybarczyk**

Revised: November 20, 2007

Purpose: The purpose of this experiment is to acquire the skill of long-term operation of an electricity generator that is based off a modification of the Linnard Griffin Electrolysis Patent.

Background: The production of hydrogen can be accomplished in several ways that include electrical and chemical means. This paper is a report on a study that used a modification of Experiment # 13 of US Patent Publication US 20060180464: "Apparatus and Method for the Controllable Production of Hydrogen at an Accelerated Rate" by Dr. Linnard Griffin.

In paragraph 41 of the patent an electrical power generator is disclosed as comprising a reaction vessel, reaction medium, anode, cathode, a colloidal metal catalyst with a high surface-area to volume ratio, and an outlet that allows the hydrogen gas to flow to a fuel cell to produce electricity. This general design was used to develop a reactor that would be used as the electricity generator reported in this document.

Electrolysis:

Hydrogen gas can be produced by a chemical reaction between water and a metal or metallic compound. These can take place in solutions that are acidic or basic in pH. such as:

$Mg + 2HCl \rightarrow H_2 + MgCl_2$ (in acidic pH medium)

$Mg + 2H_2O \rightarrow H_2 + Mg(OH)_2$ (in basic pH medium)

Due to high temperatures and activity of such reactions, and for reactions of this type in general, the efficiency (due to the consumption of one of the reactants) for such reactions increase the cost of the process required. The need for a method that produces hydrogen efficiently with inexpensive metals was greatly desired.

Linnard Griffin Electrolysis:

At the heart of this improved method of hydrogen gas production is the introduction of colloidal metal catalysts into the medium in which the electrolysis occurs.

The Nernst Equation: The Nernst equation is used to determine the relationship between the standard operating voltage of an electrical cell and the conditions under which such a cell is operating. The standard conditions are defined as: 1 molar solution at 25°C and 1 atmosphere of pressure. A cell operating under standard conditions is defined as E°. A cell voltage operating at other than standard conditions can be calculated theoretically by using the Nernst Equation:

$$E = E° - \frac{RT}{nF} \ln \frac{(\text{concentration of products})}{(\text{concentration of reactants})}$$

By using colloidal metals the concentration of the reactants becomes very large. As the concentration of the reactants increases the value for E becomes less negative. It is this reduction in the energy required that lowers the voltage required to operate the electrolysis. By using the right combinations of colloidal catalysts, metals, and reaction medium the Linnard Griffin Electrolysis Process runs spontaneously without any outside power source needed to begin and sustain the hydrogen producing reaction.
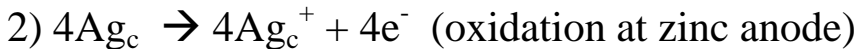
Multiple Colloidal Metals:

By the introduction of multiple colloidal metals the reaction rate can be further enhanced, and can be used to assist the regeneration of the sacrificial metal that would otherwise be consumed. As you will read later, the components of the hydrogen reactor described in this paper consist of a tungsten-carbide electrode, a zinc electrode, and a reaction medium of deionized water with sodium hydroxide, colloidal silver, and colloidal magnesium added. The resultant reactions produce hydrogen and assist in the regeneration of the zinc electrode. They follow the general cycle as described:

Assuming that colloidal silver is in ionic form once added to the reaction medium it will react efficiently with the zinc anode metal.

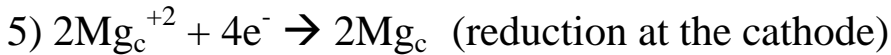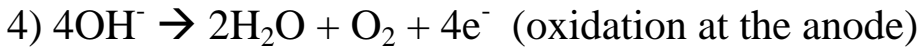1) $4Ag_c^+ + 2Zn \rightarrow 2Zn^{+2} + 4Ag_c$
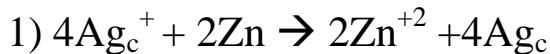
This reaction will occur swiftly because of colloidal silver's high surface area and because zinc is above silver in the electromotive series, pushing this reaction to the right side of the equation.

The reduced colloidal silver would then react with water to produce hydrogen and a base:

2) $4Ag_c \rightarrow 4Ag_c^+ + 4e^-$ (oxidation at zinc anode)
3) $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ (reduction at Cathode)

At this point in the reaction hydrogen is produced but the zinc is consumed.

With the introduction of the magnesium colloid into the reaction medium the following reduction reaction occurs at the **tungsten/carbide** electrode with the colloidal magnesium ion: Followed by the oxidation at the **zinc** anode:

4) $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$ (oxidation at the anode)

5) $2Mg_c^{+2} + 4e^- \rightarrow 2Mg_c$ (reduction at the cathode)

The magnesium colloid can then react with the zinc ion, thus regenerating the zinc.

6) $2Zn^{+2} + 2Mg_c \rightarrow 2Mg_c^{+2} + 2Zn$ (regeneration of the zinc)
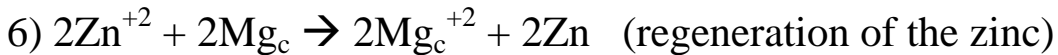
Thus starting over again at equation 1

In summary the cycle:

1) $4Ag_c^+ + 2Zn \rightarrow 2Zn^{+2} + 4Ag_c$
2) $4Ag_c \rightarrow 4Ag_c^+ + 4e^-$ (oxidation at the zinc anode)
3) $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ (reduction at the tung/carb cathode)
4) $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$ (oxidation at the zinc anode)
5) $2Mg_c^{+2} + 4e^- \rightarrow 2Mg_c$ (reduction at the tung/carb. cathode)
6) $2Zn^{+2} + 2Mg_c \rightarrow 2Mg_c^{+2} + 2Zn$ (zinc anode regeneration)

Thus back to equation one. All components being regenerated except the water which is consumed. However, in reality the regeneration of the zinc in equation 6 does not occur at a rate fast enough to regenerate the zinc as fast as it is consumed. Therefore, the zinc will eventually be used up.

The zinc can thus be regenerated by a reverse current to the zinc electrode from an outside power source.

This is essentially the Linnard Griffin electrolysis process used in this experiment. This process, as it is, will eventually consume the zinc electrode which needs to be regenerated by electrical current or replaced.

Modification of the Linnard Griffin Electrolysis Process:
Studying the process of the reaction and actually doing previous experimentation outside the bounds of this paper, it was observed that the reaction itself runs at a temperature noticeably cooler than the surrounding atmospheric temperature. This was never measured analytically, but was observed in a subjective manner by placing a hand against the reactor and feeling the coldness of the metal electrodes in contact with the reaction medium during the running of the process. This indication that the reaction runs endothermic, and further supported by the fact that increasing the surrounding temperature artificially (hot water placed around the reaction vessel surface) also increased the reaction rate; and also when the forward hydrogen production was speeded up electrically with a battery source it was found the temperature of the reaction medium dropped drastically. It was proposed that the speed of reaction 6 (regeneration of the zinc) could be increased to balance level with zinc consumption by electrical means simultaneously during hydrogen production.

Also, due to the endothermic nature of the reaction, it was proposed that energy was being absorbed into the reaction medium from the temperature differential between the medium and the surrounding atmosphere. This temperature differential represents energy that is essentially from the sun that warms our atmosphere and is energy that is constantly available for use. Just like an ice cube absorbs the energy from the warmer air around it to melt, so this electrolysis process absorbs energy from the warmer air around it to aid in powering the reaction of hydrogen production.

This energy is essentially solar energy that the reaction absorbs as heat.

The Goal:

The goal was to develop a reaction and apparatus that produced hydrogen and fully regenerated all components in the reactor at rates of consumption equal to regeneration, except the water, without any outside battery source and without any interruption in the hydrogen production.

In order to accomplish this, the first hurdle to overcome was to develop a method to regenerate the zinc as fast as it was consumed. The Linnard Griffin Electrolysis process uses two electrodes. One tungsten/carbide cathode, and one zinc anode. When electrically connected by a copper wire above the reaction medium the production of hydrogen begins spontaneously and continues as long as water is added until the zinc is fully consumed or converted into zincates. Then the reaction will stop.

The proposed modification was first the addition of a second zinc electrode into the reaction medium and a second tungsten/carbide electrode that was much smaller than the first tungsten/carbide electrode. The hypothesis is that as the larger tungsten/carbide electrode is connected to the first zinc electrode the hydrogen production will begin. Simultaneously a reverse current would be put on the remaining smaller tungsten/carbide electrode and zinc electrode so that the zinc would regenerate and release oxygen gas on this electrode as it is being consumed on the first zinc electrode.

The second part to the modification was that all electrical current would be generated by fuel cells. The experiment used two fuel cells. The first would be running a fan (this would be the energy draw) and the second fuel cell would be connected to the small tungsten/carbide and the second zinc electrode so a reverse current was regenerating the zinc. The hypothesis was that the temperature differential from the reaction to the atmosphere would absorb more energy than was expended to regenerate the zinc. This excess energy would represent energy absorbed from the atmosphere and converted into electrical energy. Just like a solar cell produces electricity from solar light energy, this reactor would produce electricity from solar thermal energy; thus, producing electricity, regenerating all components in the cell, and only consuming water.

It was further proposed that the connection to the zinc electrodes would be switched once a day so no zinc electrode would be consumed. One day it would be consumed as the reaction ran, the next day it would be regenerated; all without interruption in the hydrogen production. A reactor that produces electricity by absorbing heat from the atmosphere, and the heat would be returned to the atmosphere once it was used (in a motor, etc.); a perfect "green" cycle.

Procedure:
Assemble the apparatus described below. Connect the group of ¼" thick electrodes to one zinc electrode with a copper wire and alligator clips to begin the hydrogen generating process. Channel the hydrogen through the silicon tube into the first fuel cell, which is connected to power a fan. Channel this fuel cell outlet into the inlet port of the second fuel cell. With a copper wire and alligator clips attach the negative side of the second fuel cell to the zinc anode to be regenerated. Connect the positive side of the fuel cell to the small 1/16" tungsten cathode used for regeneration. The current will regenerate the zinc anode.

Every twelve hours the connections to the zinc electrodes should be switched so that the other zinc electrode will regenerate. Every 24 hours hydrate the fuel cells by flushing with de-ionized water and blowing excess water out of the cell.

Record the voltages across the fan several times a day and across the regeneration fuel cell as well. Add de-ionized water to the reactor as needed to maintain water level.

Run as long as possible and record all observations.

Materials:
1 – Fan for Fuel Cell Demo. Item# 591107
2 – One Foot section of 3/16" Silicon Tubing Item #591363
2 – Fuel Cell Eco H_2/ Air – Item #40-534607
From   www.fuelcellstore.com

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10 - Tungsten/Carbide electrodes (0.250 O.D. X 5.00 L)
 Grade IC 6S
From: www.innovativecarbide.com

0.250 Thick #3030 Green Extruded Acrylic Panels
 7 --- Size (3" X 6")
 2 --- Size (3" X 3")
From: www.professionalplastics.com

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2 – Stainless Steel ¼" gas ports
From Menard's Hardware

Sodium Hydroxide Flakes
Potassium Hydroxide Flakes
From: www.aaa-chemicals.com

Silver and Magnesium colloids

From: www.wateroz.com
> ---

Commercial Zinc Rod (3/8" X 12")
From: www.boatzincs.com
> ---

4 - #2 rubber stoppers. Three with holes and the fourth a solid stopper with a hole drilled into it just large enough to accommodate the 1/16 " diameter tungsten rod.
From: Any laboratory supply house. The ones I used were lying around the laboratory for the last 20 odd years or so.
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Apparatus:
The apparatus design was based on the need for a reactor that had two chambers, one for hydrogen generation and one for oxygen generation. The chambers needed to have an ability to exchange ions back and forth, but the mixing of gases had to be prevented because of the use of the fuel cells. Any oxygen that contaminated the hydrogen side of the reactor or leaked into the hydrogen side of the fuel cell would reduce the efficiency of the output of the cell and possibly even stop electrical output.

Another consideration was the need for two separate zinc rods and two separate tungsten/carbide rods as well. This was so one zinc-tungsten/carbide connection could be used to generate hydrogen and the other set would be used to regenerate the zinc electrode and liberate the oxygen. So a small 1/16" tungsten rod was chosen to be used for all regeneration, and the other group of tungsten/carbide electrodes (10 of them) would be used to produce hydrogen constantly. All rods in the group were physically connected by touching each other. To meet all these needs the following design was chosen:
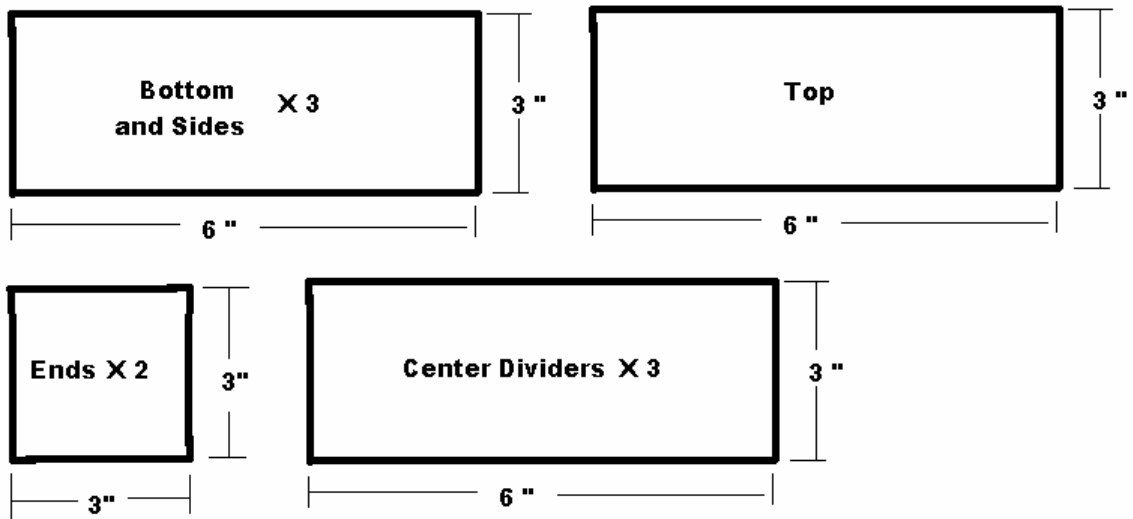
Diagram 1

All Plexiglas sheets were of ¼ " thickness.
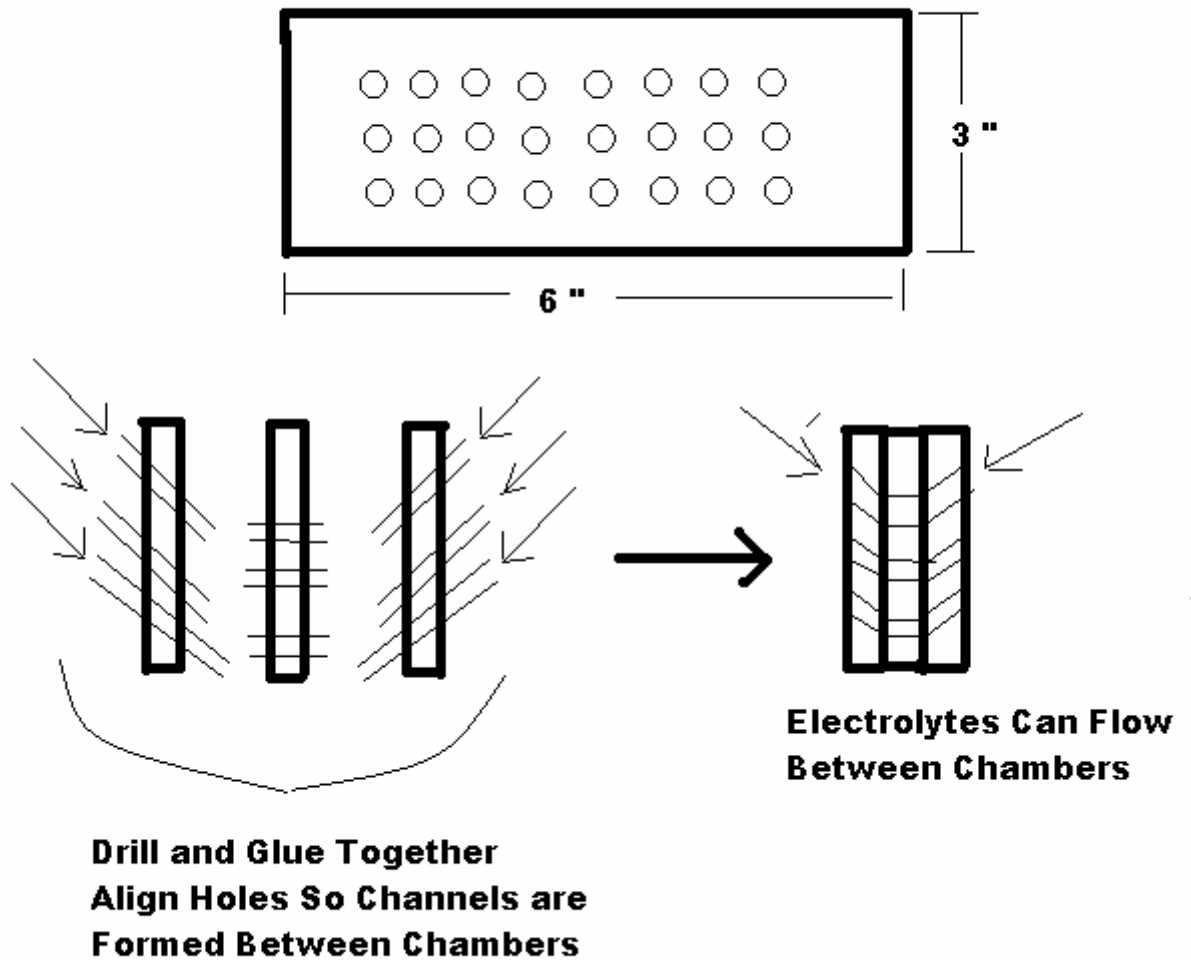
Drilling Holes in the Center Dividers

3 "

6 "

Drill and Glue Together
Align Holes So Channels are
Formed Between Chambers

Electrolytes Can Flow
Between Chambers

Diagram 2

This way no gas would pass between the chambers, but the electrolyte could.

All Electrodes Through Rubber Stoppers

Tungsten/Carbide Electrodes Hydrogen Production

Zinc Electrodes Oxygen Production

Reactor End View

Diagram 3

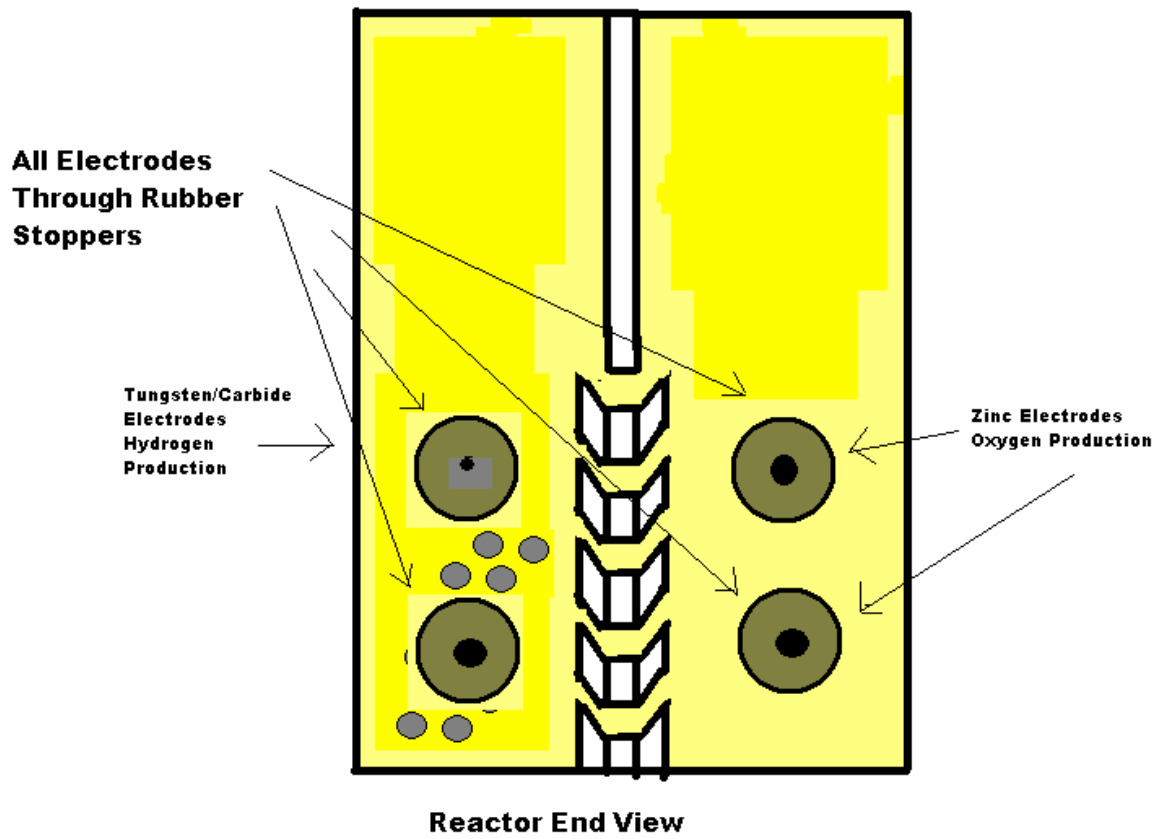Small (1/16") Tungsten Rod   Rubber Stoppers
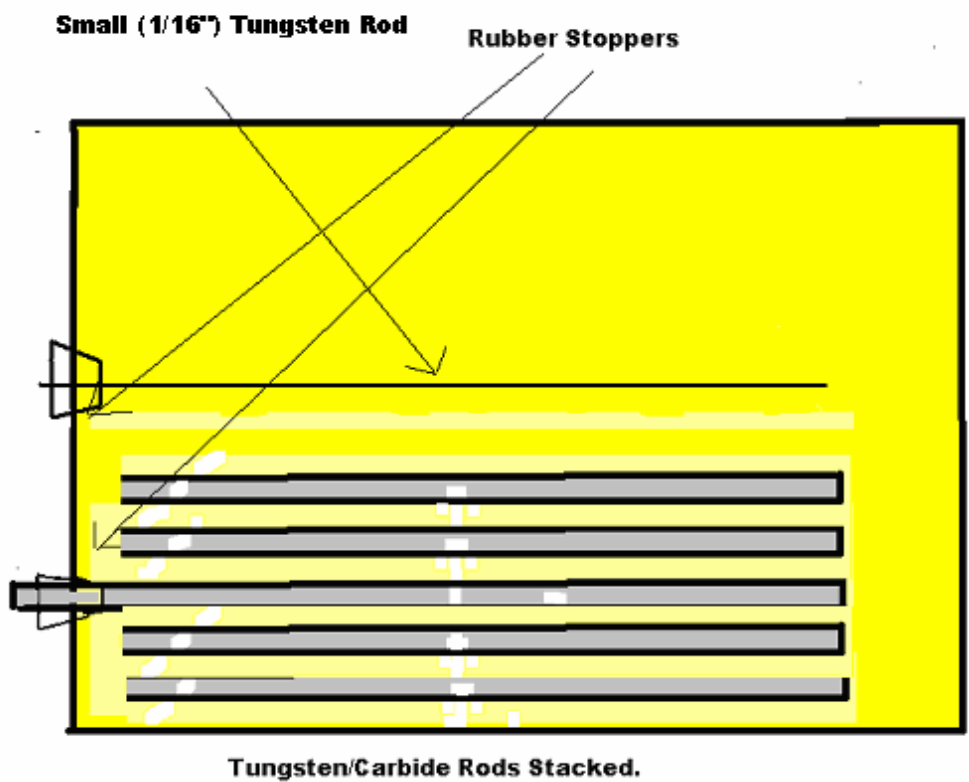
Tungsten/Carbide Rods Stacked.

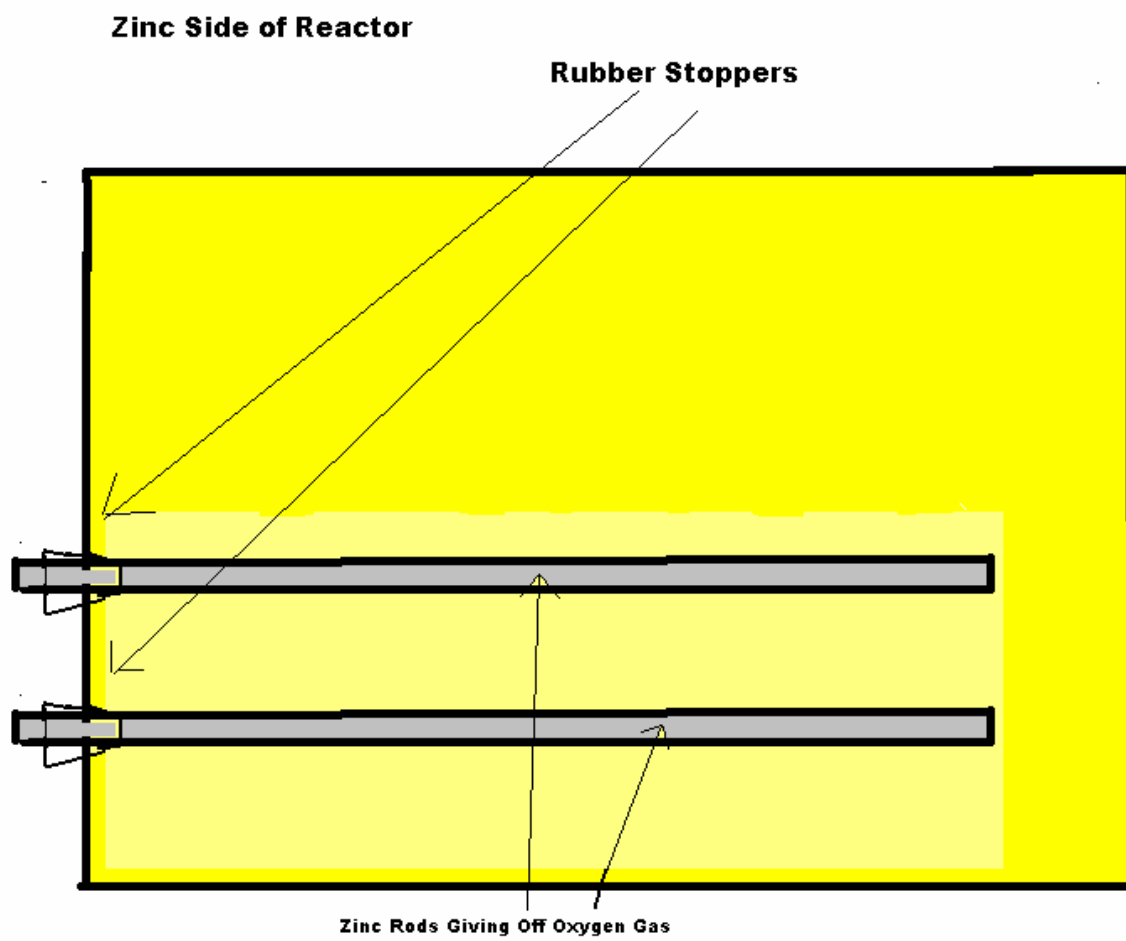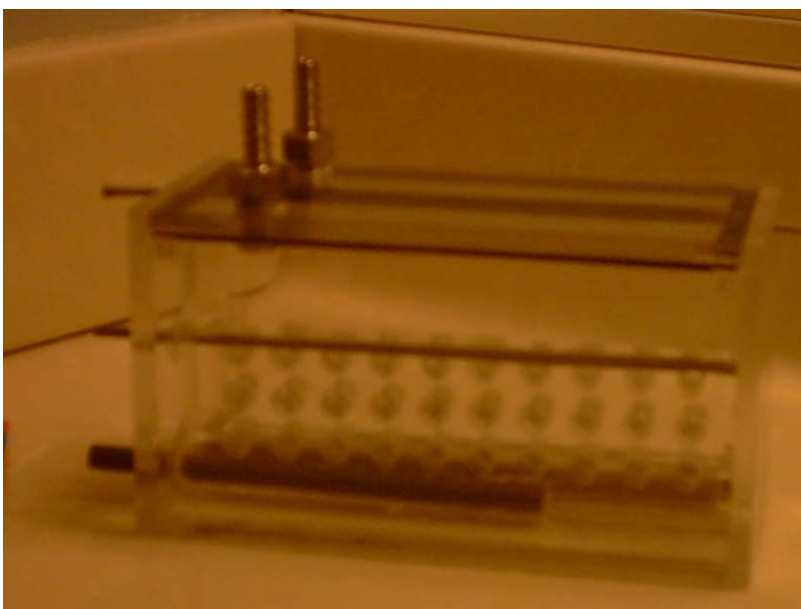**Diagram 4**

Diagram 5

Here are a few pictures of the reactor before the zinc anodes and rubber stoppers were installed.

Picture 1

Picture 2

Picture 3

Two gas ports were put in the lid. One on the oxygen (zinc) side and one on the hydrogen (Tungsten/Carbide) side.

The reactor was glued together using methylene chloride. Any cement that works on Plexiglas should work.

Electrolyte Solution:
Into a thick glass beaker place 200 ml of de-ionized water. Place this into a cold water bath to control the exotherm that will result when the hydroxides are dissolved. Wearing safety glasses, latex gloves, and working with good ventilation, dissolve 40 grams of potassium hydroxide with stirring. (Warning: solution will get hot). Once the solution cools, dissolve 40 grams of sodium hydroxide powder with stirring. (Warning: solution will get hot! Avoid breathing fumes!!). Once dissolved add 80 ml of 20 ppm silver colloid and 40 ml of 20 ppm magnesium colloid. Bring the volume to a total of 400 ml with de-ionized water. (Warning: solution will again exotherm and get hot!). Mix until cool.

Add to the reactor and seal it.

Add the fuel cells as shown.
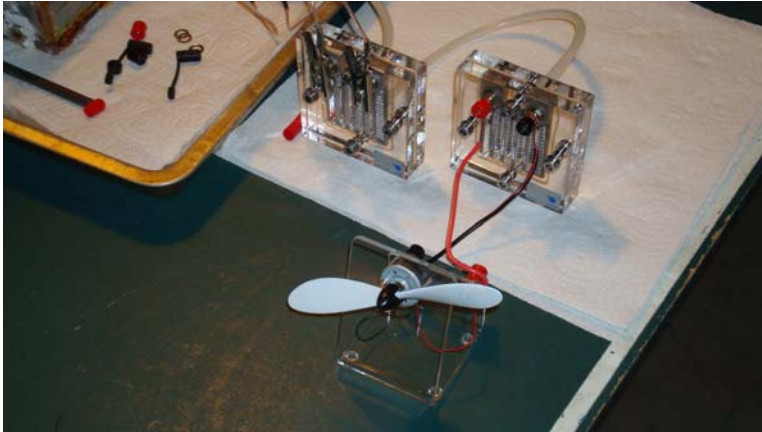
Picture 4

The first fuel cell is being used as the regeneration power. The negative side of the output is attached to the zinc electrode to be regenerated and the positive side of the fuel cell is attached to the small tungsten electrode. This should regenerate one zinc electrode at a time.

The other connection is the tungsten/carbide electrode group to be used for hydrogen generation to the other zinc electrode that is not regenerating. Connections are made with copper wire and alligator clips.

Results:

At the beginning of the reactor run the initial readings were:

Fan voltage: 0.762 volts at 50mA
Regeneration: 0.870 volts at 3.39 mA.

After 74 hours of operation the readings were:

Fan Voltage: 0.674 volts at 41.4mA
Regeneration: 0.826 volts at 3.44mA

After 156 hours of operation the small tungsten electrode started to form yellowish precipitate on its surface.

After 179 hours of operation the readings were:

Fan Voltage: 0.712 volts at 50mA
Regeneration: 0.858volts at 4.5mA

After 200 hours the yellowish precipitate was forming on the top surfaces of all the electrodes; both tungsten/carbide and zinc.

After 331 hours the color of the electrolyte started to take on a greenish tinge.

Fan Voltage: 0.672 volts.
Regeneration: 0.776 volts.

After 363 hours the fan started to run with intermittent stopping, then starting again.

Fan Voltage: 0.670 volts
Regeneration: 0.750 volts

At 366 hours the fan was switched to the first fuel cell so it had the main draw.

Fan Voltage: 0.690 volts.
Regeneration: 0.698 volts

At 402 hours the fan was running fine:

Fan Voltage: 0.730 volts
Regeneration: 0.691 volts.

At 407 hours it looked like the regeneration dropped off:

Fan Voltage: 0.713 volts
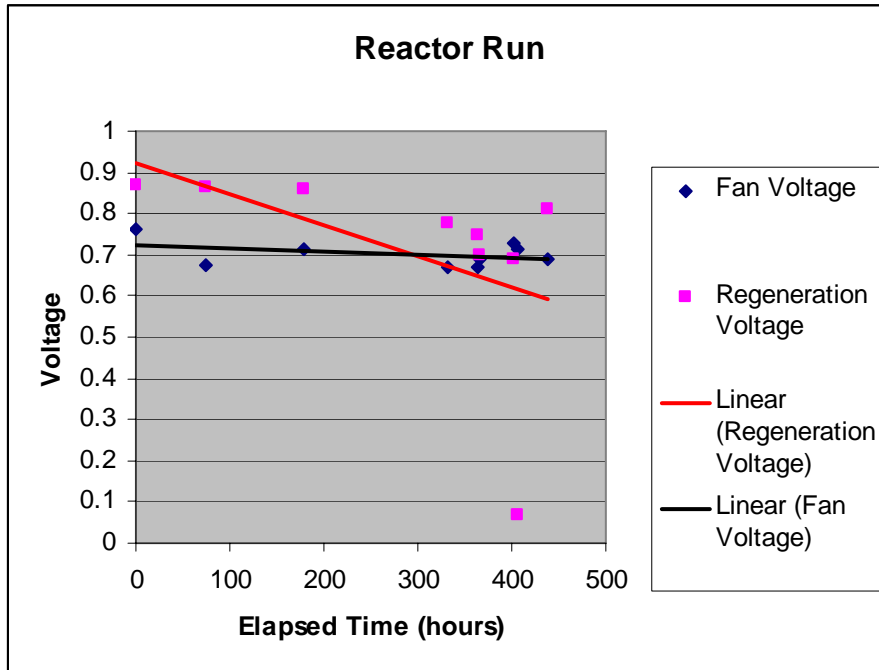Regeneration: 0.068 volts

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At 438 hours it was discovered that the small tungsten electrode was touching the larger tungsten/carbide group of electrodes that was producing the hydrogen, effectively shorting out. A rubber band was used to put separating pressure on the electrodes and was able to separate them.

Fan voltage: 0.691volts
Regeneration: 0.810 volts.

At 455 hours the reactor electrolyte had a greenish hue and a precipitate covered all the electrodes. It was still giving off hydrogen and regenerating but the fan only ran intermittently.

Hydrogen still seen bubbling at a rate of about 4-5 bubbles/second.

At 475 hours the regeneration and the fan were no longer able to run at the same time. The output of the gas had dropped to the point where only the fan could be running, or the regeneration could be running. The experiment was terminated at this point and the unit was disassembled and the electrodes examined.

Looking at the general trend lines the fan voltage draw remained on average steady at around 0.7 volts while the trend line of the regeneration voltage draw was a declining line over the reactor run. Unfortunately the shorting of the reactor from hours 407 to 438 for over 30 hours by the touching of the hydrogen producing and regeneration tungsten electrodes hurt the regeneration output and damaged the total output of the reactor from that point on.

Picture 5
tungsten (thoriated) (1/16" diameter) on left
Tungsten/carbide (1/4" diameter) second from the left

Both electrodes (as well as all the tungsten electrodes in the reactor) had a precipitate coating on their surface. This most likely formed when the voltage output of the fuel cells began to drop as a result of the shorting out of the tungsten and tungsten/carbide electrodes that occurred between 407 and 438 hours of operating time.
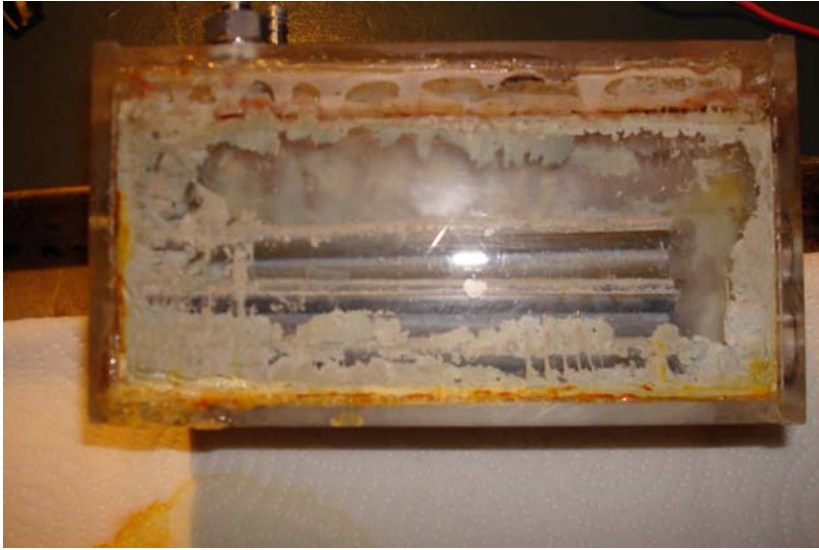
Picture 6
Two Zinc Electrodes on Right

Notice that the two zinc electrodes both have the jagged surface with imperfections, indicating uneven plating. There is also appearance of a zincated coating on the right electrode. Most likely caused during lower voltages of regeneration. Probably also resulting from the lower voltages during the period the reactor was shorted on the tungsten/carbide electrode side.

Picture 7

The two zinc electrodes on the right were from an experiment that was performed previously. These are two zinc rods that resulted from an overnight run of another separate cell. Notice that these two electrodes are only slightly larger than the next two electrodes that came from the reactor after a 20 day run. This indicates that the electrodes in the 20 day run were regenerating. Otherwise the electrodes would have been completely consumed in the reaction.

Picture 8

Tungsten/carbide (hydrogen generation) side of the reactor after the end of the run. Notice the precipitate on the tops of the electrode and on the plexiglas sides of the reactor. This precipitate most likely damaged output of the reactor and slowed down hydrogen production.

Picture 9

Zinc (oxygen) side of the reactor also had the precipitate on the electrodes and sides of the reactor.

The importance of keeping the regeneration voltage above 0.83-0.85 volts seemed to be a defining moment in the clarity of the cell.

Calculations: The total amount of energy required to regenerate the electrode is defined as the regeneration energy usage. This was determined as in the example at 170 hours. Fan Draw: 0.712 volts @ 50mA and the Regeneration Draw was 0.858 volts @ 4.5mA. So the amount of energy used by the regeneration is:

$$\frac{(\text{Regeneration Draw})}{(\text{Fan Draw} + \text{Regeneration Draw})} \times 100 = \% \text{ of total energy for Regeneration}$$

As at 170 hours

$$\frac{(0.858 \text{ volts} \times 0.0045 \text{amps})}{((0.712 \text{volts} \times 0.050 \text{amps}) + (0.858 \text{ volts} \times 0.0045 \text{amps}))} \times 100 = 9.8\%$$

So the total amount of energy used for regeneration is approximately only 10% of the total output of the fuel cells.

Conclusion:
In conclusion it has been shown that the Linnard Griffin process can be modified to regenerate the zinc electrode as the hydrogen is being produced in a long-term operation of a hydrogen-based electricity generator.

Discussion and Sources of Error:
Based off the results the amount of energy required to regenerate the zinc is about 10% of the total output of the fuel cells. Considering that fuel cells are about 50% efficient, the incorporation of the platinum wires directly into the cell would greatly improve the output of the reactor.

It would seem that the reactor was running in a shorted-out state when the tungsten electrodes for both fan and regeneration were touching from hours 407 to 438. The cell really took a beating on precipitate and color and clarity during that time. What kind of damage might have been done to the system is not fully known, but the short was not easily noticeable.

The reactor was still giving off gas when the experiment was ended but not as well as at the beginning. It is believed that the switching of the zinc connections every 12 hours made the difference as the cell ran longer and stayed cleaner than the first run where the connections were switched every 24 hours.

This was a good long run and with only 10 tungsten/carbide electrodes inside the reactor it has done well and taught how to maintain its output.

During the run the zinc connections were switched every 12 hours and the fuel cells were hydrated and switched with each other every 24 hours.

This shows that further study can adjust reactor operating parameters to extend the reactor running time even further.

Scale-up:
The next reactor will be built at about the size of a small microwave oven. It will incorporate 80 tungsten/carbide electrodes and will surround the two zinc electrodes with tungsten/carbide electrodes on all sides. Also two 1/16 " diameter tungsten rods will be incorporated instead of just one for regeneration. These electrodes will be placed on opposite sides of the reactor. The purpose of this is to avoid the reddish-yellow precipitate from accumulating on one of the small electrodes. If they are switched along with the zinc connection then it should avoid forming precipitate on these electrodes and keep the cell running longer.

Further plans are to incorporate platinum wires directly into the cell or above the cell in a separate chamber filled with de-ionized water so electricity would be produced without even having to let the hydrogen gas escape. This will eliminate the need for an external fuel cell.

References:
US patent 2006 0180464 "Apparatus and Method for the Controllable Production of Hydrogen at an Accelerated Rate. August 17, 2006

Chemistry A Modern Course
Smoot – Price
Copyright 1975
Charles E Merrill Publishing Co.
Columbus, Ohio 43216