HYDROGEN GENERATION VIA WATER ELECTROLYSIS USING HIGHLY EFFICIENT NANOMETAL ELECTRODES

April 2007

Robert B. Dopp[1]

ABSTRACT:

Energy supplies in the 21st century will be challenged as fossil fuel reserves decline, human consumption increases, and greenhouse gasses accumulate to further damage the atmosphere. These challenges will be met by innovative solutions that enable the hydrogen economy; to replace petrochemical fuels with hydrogen for use in fuel cells and internal combustion engines. One of the most difficult challenges is to produce hydrogen at a cost competitive with current fuel pricing (fossil or natural gas). DoppStein Enterprises (DSE) and QuantumSphere Inc. (QSI) have developed a disruptive technology to increase the efficiency of water electrolysis, utilizing its capability to manufacture high surface area nanometal particles (3-50 nm) by a scalable process.

To accelerate adoption of the Hydrogen Economy, hydrogen must be produced from a clean source and at rates and efficiencies competitive to gasoline. DSE has developed a unique electrode structure for alkaline water electrolysis by capitalizing on the enhanced surface area and catalytic reactivity of QSI-Nano® catalysts in a fluidized bed reactor (FBR) design ***which exceeds a rate of 5 amps/cm^2 at 93% energy efficiency. This is equivalent to 2 gge/hr/m^2, 21 NM^3/hr/m^2 and 42 kWh/kgH$_2$.***

DSE

---

[1] Robert is a Technical Liaison to QuantumSphere, Inc.
DoppStein Enterprises, Inc. , 1925 Fields Pond Glen, Marietta, GA, 30068, (phone) 770-649-1933 (email) rbdopp@doppstein.com (web) www.doppstein.com
QuantumSphere, Inc., 2905 Tech Center Drive, Santa Ana, CA 92705, (Phone) 714-545-6266 (email) kmaloney@qsinano.com (web) www.qsinano.com

For the mathematical background, see **Appendix 1** below where the algorithmic logic and assumptions made in the calculations used in this paper are explained.

1.4 DoE Targets

The 2010 DoE target is to exceed 75% energy efficiency for the total plant, but it can be assumed that even in a well designed electrolysis apparatus, about 8% of the energy is lost to parasitic losses such as heating, pumping, valves, sensors and controllers within the system. In this work, we are assuming a 10% loss, so we are targeting an 85% efficiency. This gives an operating cell voltage of 1.743V. **Figure 2** shows the relationship between full cell voltage and the Energy Efficiency of the cell.

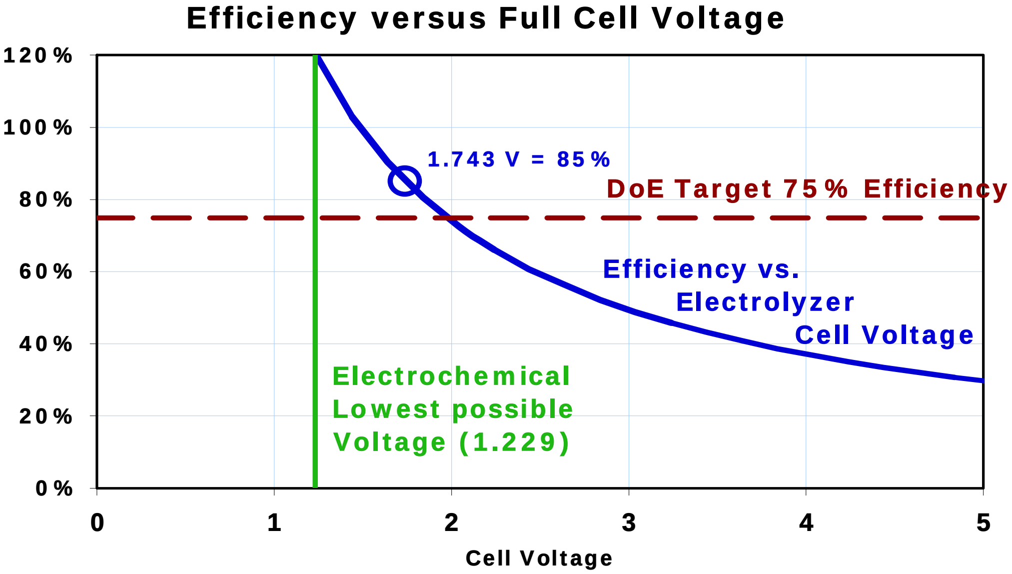

Figure 2. Cell efficiency versus cell voltage with respect to the DoE energy efficiency target.

2. PRINCIPLES OF ELECTROLYSIS

Water electrolysis to produce hydrogen and oxygen is an old technology originating in the early 19th century shortly after Volta introduced the first battery in 1800. The principle chemical equations are shown in **Figure 3,** where the electrochemical flow is shown for acidic and alkaline environments. This work involves the alkaline reaction pathway.

Water Electrolysis

Net Reaction: $H_2O \text{ --> } H_2 + ½\, O_2$

Acidic Reaction	**Alkaline Electrolysis**
Anode: $H_2O \text{ --> } ½O_2 + 2H^+ + 2e^-$	$2OH^- \text{ --> } ½O_2 + H_2O + 2e^{--}$
Cathode: $2H^+ + 2e^- \text{ --> } H_2$	$2H_2O + 2e^- \text{ --> } H_2 + 2OH^-$

Figure 3. Electrochemical pathway for acid and alkaline electrolysis.

To understand the principles of electrolysis, perhaps the most basic experiments is the use of two pencils sharpened at both ends with the top being connected to a battery and the bottoms inserted into alkaline water. **Figure 4** illustrates the concept showing many bubbles appearing at the negative pencil and half that many appearing at the positive. The reactions are:

Positive: $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

Negative: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

This is the same principle of even the most sophisticated water electrolysis machines with the difference being in efficiency and production rate as discussed below.

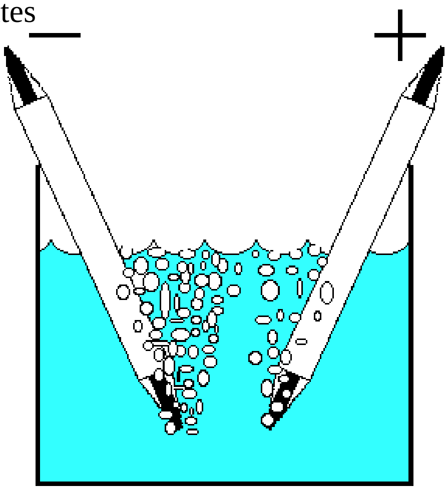

Figure 4. Pencils used to illustrate the principle of electrolysis.

3. NANOPARTICLE SURFACE AREA EFFECT

As a material is divided into smaller and smaller particles, the three dimensional surface area per gram increases logarithmically. For example, a one gram pellet of nickel is 0.6 cm in diameter and has a surface area of 1.12 cm^2, or about that of a fingernail. A 10 nm particle has a surface area of 67 m^2 per gram or 27 feet on a side - a 60,000,000% increase.

The two dimensional surface area of any geometric surface view is, however, unchanged as the particles become smaller. Imagine peering through a tube at a collection of marbles. As the marbles become smaller (but still filling the view space), the viewable surface is unchanged regardless of how small the particles become. However, mixing micron and nano powders have a profound effect on the surface area as viewed through a fixed geometric surface area. In early experiments, electrodes were made using a 20 µm powder mixed with 10% nano powders which were about 10 nm. This combination increased the two-dimensional surface area by about 2000%. An electrochemical event is usually two dimensional because the ions are flowing toward the electrode in laminar lines and therefore strike the reactive surface like rays of light would when beamed from a flashlight.

As particles get smaller, the percent of atoms on the surface increases dramatically. A one µm particle, for example has only 0.15% of the atoms on the surface. A 10 nm particle is up to 14% surface atoms, and a one nm particle has 87% of its atoms residing on the surface of the particles. An atom in the bulk of a metal has 12 immediate neighbors. A surface atom has from 6 to 9 neighbors, so there are electron fields that penetrate the reactive boundary layer. Therefore, the one nm particle has a much higher surface energy than larger particles.

4. POROUS 2-D ELECTRODES USING NANOCATALYST

Pellets were made by first mixing micron-sized nickel powder with QSI-Nano® catalysts, followed by compression and sintering. **Figure 5** illustrates the resulting electrode and magnified surface views. Ions flow at normal angle to the pellet and gasses are expelled from the same surface. This requires pumped electrolyte to constantly sweep the electrode with de-gassed electrolyte to prevent masking of the electrode. The pellets were tested in a half-cell apparatus which used a platinum screen as a counter electrode and a separator between the oxygen and hydrogen chambers made of reformed cellulose (cellophane).

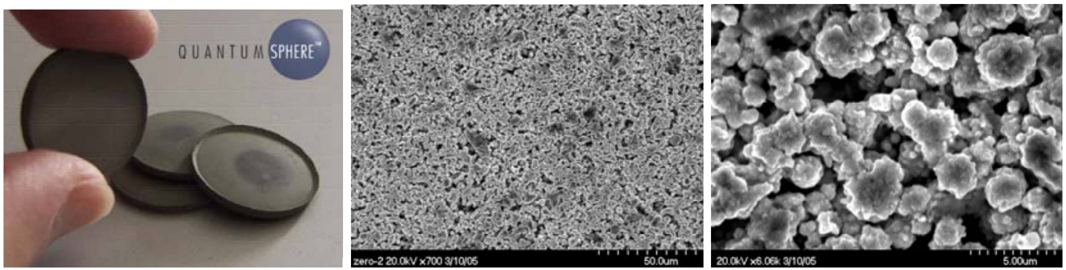

Figure 5. Electrodes containing QSI-Nano® catalyst and magnified view of porosity.

Test materials included graphite, micron nickel, micron nickel with 10% nano nickel, and micron nickel with 10% nano catalyst mixture of three catalysts. **Figure 6** shows a full voltammogram of the anode (oxygen generating) and cathode (hydrogen generating) scans combined. The difference between these lines defines the cell voltage. Shown is also a double-headed arrow showing the 85% energy efficiency potential (1.743 V). It is clear that in all designs, the 85% Energy Efficiency level is reached, but at different rates. Even the graphite lines reach that potential at just 3 mA/cm^2 current density.

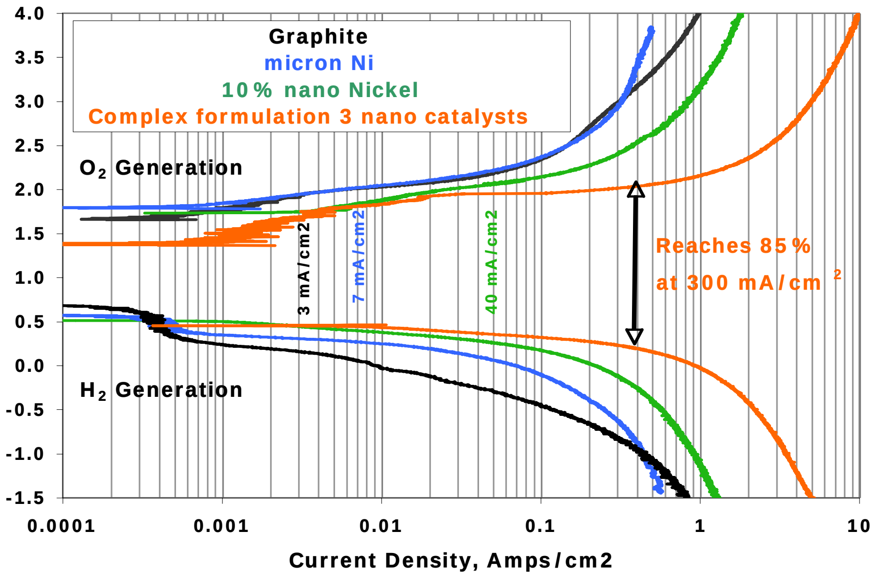

Figure 6. Voltammogram comparing high surface area electrodes with lower surface area electrodes.

Note the improvement between the micron nickel lines (blue) and the 10% nano nickel lines (green), where about a six fold improvement is observed. This can be called the "nano-effect", and demonstrates the effect of a 2000% increase in surface area surface activity. The triple catalyst (orange) lines show how combining the high surface area with thoughtful chemical engineering can give a hundred fold improvement over graphite.

Current density data in **Figure 6** can be converted through simple unit conversion to a production rate of gge/hr/m^2 or the amount of hydrogen that can be produced in one hour if the electrode were one square meter. **Figure 7** compares the pellet experiments on this parameter. Also included are production rates translated to ml/hr/m^2 for easier comparison. The triple nano catalyst design is 100 times higher rate than graphite.

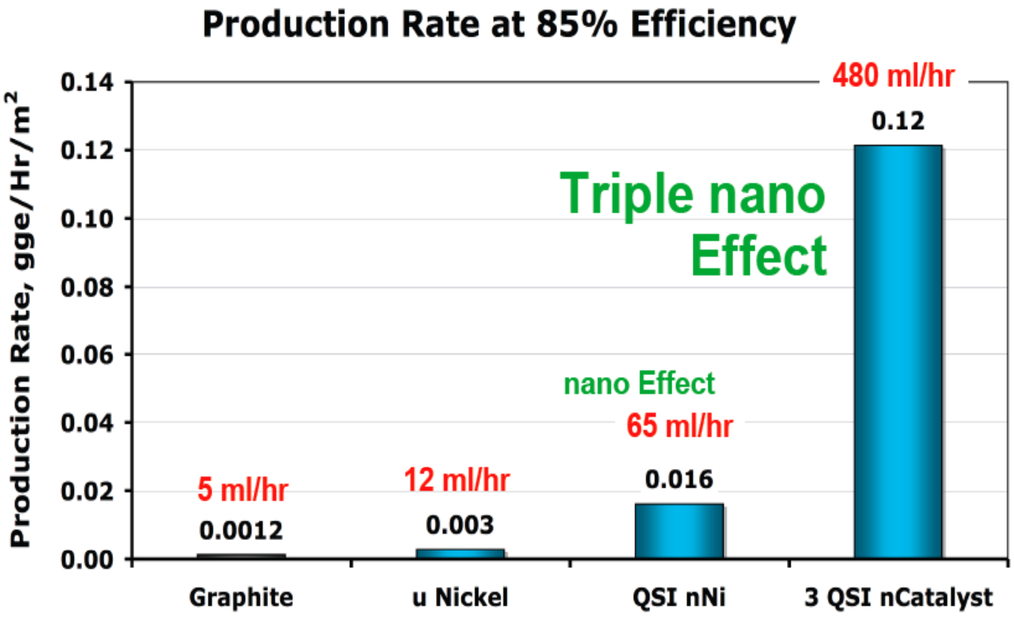

Figure 7: Effect of nanocatalysts in hydrogen electrodes at 85% efficiency.

5. FLUIDIZED BED ELECTROLYSIS (3-D)

Although the pellet design shows remarkable efficiency even before optimization, some difficulties were observed. The pumped electrolyte showed that some of the nano catalyst had sloughed off, despite the sintering process. Also, internal resistance was evident due to compression differences of various powders. Finally, because the electrodes face each other and the ions pass through the gas bubbles, pumping is required and spacing of the electrodes must be enough to allow the flow of electrolyte.

A solution to these issues was demonstrated in half-cell experiments by rotating the electrode to a horizontal position and bringing the ions in from the bottom as the hydrogen is allowed to freely escape upward. The nano particles are drawn upward with the hydrogen bubble, but a sister particle immediately replaces it, continuing the reaction. It became clear that a fluidized bed was established where a third dimension was added to the reaction space. In a fluidized bed reactor (FBR), electrons flow into the bulk of the electrolyte, where catalytic particles and ion soup producing a remarkably high rate. This allows for an enormous three dimensional surface area and surface energy, which leads to a three-dimensional reaction zone and highly efficient electrolysis at practical rates.

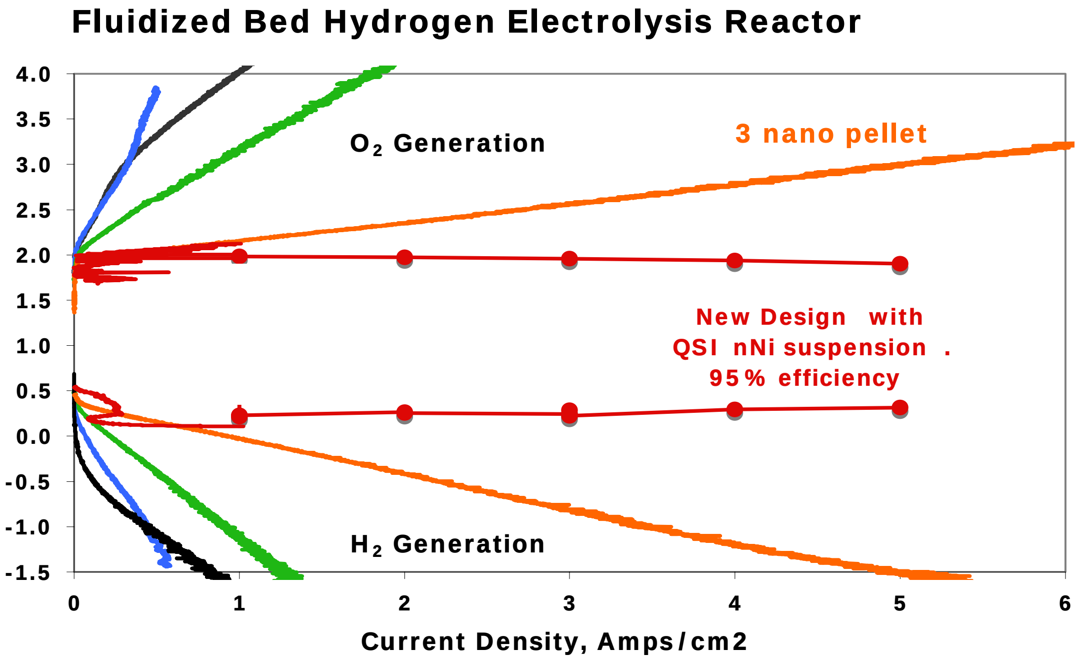

Figure 8. Polarization curve of a fluidized bed reactor plotted over the pellet data.

Figure 8 shows a Polarization curve which uses a linear x-axis to compare the pellet data with this new FBR data. What this graph is demonstrating is the development of a Fluidized Bed. As currents increase, the bed becomes more stable and more conductive to electrons, increasing the three dimensional nature of a FBR. For each geometric cm^2 of current collector on the x-axis, there is progressively deeper penetration of the electrons and greater 3D functionality of the system. This resulted in ever improving efficiency as currents increased. At 5 Amps/cm^2, the separation of the oxygen and hydrogen curves was only 1.59 volts ideal or 93% energy efficient at a production rate of 42 kWh/kg.

Figure 9 compares the results of these experiments on a logarithmic production rate scale. This way, even the low rate graphite can be compared with the FBR data. Also shown is the reciprocal number of days to produce one gge if the electrode were 1 m^2.

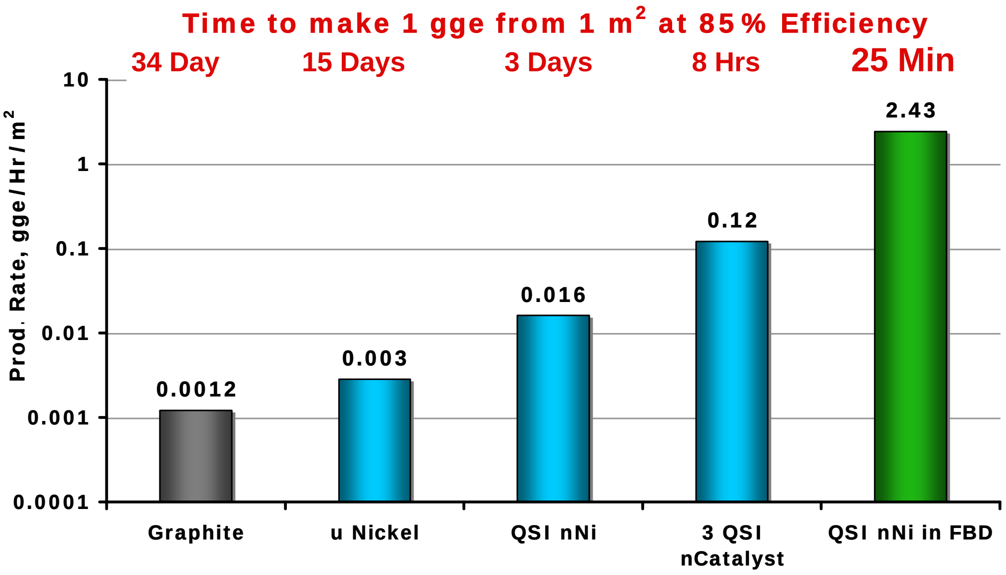

Figure 9. Production rate comparison of electrolyzer data.

6. CONCLUSIONS

- **Utilizing QSI-Nano® catalysts in a fluidized bed reactor (FBR) design resulted in an electrolyzer with 93% at 5 A/cm^2**
- **In an FBR, efficiency increases as current is increased; upper limiting current density has not been determined yet**
- **Through the use of practical operating current, clean hydrogen can be produced at least 20 X faster compared to a traditional electrolyzer, and also use less energy**
- **Further refinement of catalyst, pressure, temperature, electrolyte, and separator will yield further improvement.**

7. FURTHER INFORMATION

Funding and materials for this research was kindly supported by QuantumSphere, Inc. Several patents are pending on this and related technologies.

QuantumSphere, Inc

QuantumSphere (QSI) is a manufacturer of nanoscale catalyst materials for applications in portable power, renewable energy, electronics, aerospace, defense and other markets demanding advanced materials. QSI's proprietary technology enables the production of ultra-pure, highly uniform nanometals and alloys under 100 nanometers in high volume at commercial prices with the potential to be utilized in a large number of new applications. QSI has also created an extensive intellectual property portfolio around its process capabilities and end-use commercial applications. QSI seeks to leverage its market position to manufacture and ship QSI-Nano® catalyst materials and electrode devices for clean-energy applications such as high-performance batteries and micro fuel cells for portable power, and hydrogen generation through electrolysis, among others. The current global catalyst market is in excess of $10 billion, annually.

QSI also has collaborative agreements with industry experts, national labs, and leading universities to leverage QSI-Nano® catalyst materials in multiple additional applications and generate licensing rights to resulting intellectual property.

For more information, visit www.qsinano.com or contact Kevin Maloney at kmaloney@qsinano.com or phone 714-545-6266.

DoppStein Enterprises, Inc.

Robert Dopp is President of DoppStein Enterprises, Inc., Marietta, GA, where he consults to fuel cell, battery and materials companies. He offers a depth of knowledge in battery systems with freedom and flexibility from his independent laboratory. His proficiencies include fuel cells, hydrogen generation and water desalination. He is one of the foremost authorities on Zinc Air with 36 patents and 6 pending in energy related fields. Robert was principal engineer at Rayovac Corporation for 18 years on the Zinc Air project with a variety of leadership responsibly. As “Director of Research” for Electric Fuel Corporation working from his personal laboratory directing research in Biet Shemish, Israel, he was instrumental in developing components resulting in batteries with over four times the energy density of alkaline cylindrical cells. Since being independent, he has worked in many aspects of the electrochemical world.

For more information, visit www.doppstein.com or contact Robert Dopp at rbdopp@doppstein.com or phone 770-649-1933.

Appendix 1. MATHEMATICAL BACKGROUND and TARGETS

1.1 Energetics

The energy contained within the hydrogen generated (H_2gen) can be calculated by employing Faraday's electrochemical law and the higher heating value of hydrogen (HHV = 134.4 BTU/gH2).

$$BTU_{h_2gen} = \left(\frac{Amp * Hours}{F * 2} * H_2gmw \right) * \frac{BTU}{gH_2} \quad \textbf{(1)}$$

$$BTU_{h_2gen} = \left(\frac{Amp * Hr * 3600 \frac{Sec}{Hr}}{96487 \frac{ASec}{eq} * 2 \frac{eq}{mol}} * 2.0159 \frac{gH_2}{mol} \right) * 134.483 \frac{BTU}{gH_2} \quad \textbf{(2)}$$

$$BTU_{h_2gen} = AHr * 5.058 \frac{BTU}{AHr} \quad \textbf{(3)}$$

This then gives the BTU in hydrogen per Amp-hour. Using Ohm's Law, we can calculate the energy required to electrolyze water, expressed with the units of Watt-hours.

$$BTU_{used} = (Amp * CellV * Hr) * \left(\frac{BTU}{WHr} \right) \quad \textbf{(4)}$$

$$BTU_{used} = (WHr) * \left(3.413 \frac{BTU}{WHr} \right) \quad \textbf{(5)}$$

The energy efficiency of the reaction is then simply expressed as the ratio of **(3)** and **(5)**:

$$EnergyEfficiency = \frac{BTU_{h_2gen}}{BTU_{used}} \quad \textbf{(6)}$$

Or, preserving units:

$$EnergyEfficiency = \frac{\left(\frac{Amp * Hr * 3600 \frac{Sec}{Hr}}{96487 \frac{ASec}{eq} * 2 \frac{eq}{mol}} * 2.0159 \frac{gH_2}{mol} \right) * 134.483 \frac{BTU}{gH_2}}{(Amp * V * Hr) * \left(\frac{BTU}{WHr} \right)} \quad \textbf{(7)}$$

$$EnergyEfficiency = \frac{Amp * Hr * 5.058}{(Amp * V * Hr) * 3.413} \tag{8}$$

$$EnergyEfficiency = \frac{1.482}{CellVoltage} \tag{9}$$

Notice that Energy Efficiency is dependant only on the reciprocal cell voltage.

1.2 GGE and Production Rate

Gallon of gasoline equivalent (gge) refers to the amount of hydrogen which is energy equivalent to one gallon of gasoline. Coincidentally, one gge is nearly equivalent to one kilogram of hydrogen, so it may also be utilized as a gravimetric unit. The energy value of gasoline greatly depends on the grade and testing facility, but the average value calculated by the US Department of Energy is about 125,000 BTU's.

$$GallonsofGasEquivalent = gge = 125{,}000 BTUH_2 \xrightarrow{About} 1kG_{H2} \tag{10}$$

For a convenient method of comparing production rate, the unit **gge/hr/m^2** is employed. Simply stated, it is the gallons of gasoline equivalents that could be produced from a 1 m^2 electrode:

$$\textbf{Production Rate as } gge/Hr/m^2 = \frac{Amp}{cm^2} * 0.405 \tag{11}$$

Note that hydrogen production rate **(11)** is not related to the reaction efficiency. But one needs to consider at what efficiency the current is being delivered. This paper uses 85% energy efficiency for all comparative discussions.

1.3 Cost Efficiency

The most useful way of rating the efficiency of a hydrogen generator is by calculating the energy required to make one kg of hydrogen. If the cost of electricity is known, it is simple to convert to the cost of a kg of hydrogen, essentially the cost of a gge.

$$\frac{kWhr}{kg} = \frac{Whr}{g} = \frac{Amps * CellV}{\left(\frac{Amp * Hr * 3600 \frac{Sec}{Hr}}{96487 \frac{ASec}{eq} * 2 \frac{eq}{mol}} * 2.0159 \frac{gH_2}{mol} \right)} \tag{12}$$

$$\frac{kWhr}{kg} = \frac{Whr}{g} = \frac{Amps * CellV * 96487 \frac{ASec}{eq} * 2 \frac{eq}{mol}}{\left(Amp * Hr * 3600 \frac{Sec}{Hr} * 2.0159 \frac{gH_2}{mol} \right)} \tag{13}$$

$$\frac{kWhr}{kg} = \frac{CellV}{\left(cm^2 * Hr\right)} * 26.5905 \tag{14}$$

Cost per unit is commonly described with respect to \$/gge. Using this unit is ambiguous due to the fact that it is highly dependent on the cost of electricity. This makes it difficult to critically evaluate data across different systems if baseline electricity cost is not disclosed. **Figure 1** is an illustration of this, where 85% efficiency is assumed. The cost per gge is anywhere from \$1.90 to \$9.25 depending on whether the cost of electricity is the industrial rate in Georgia or California.

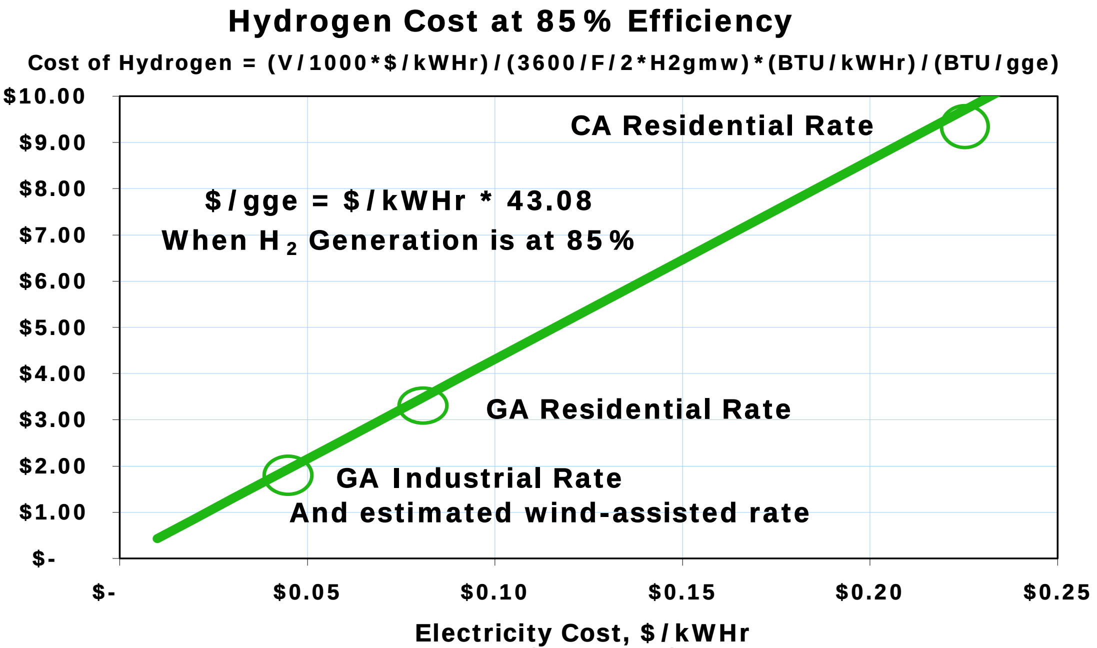

Figure 1. Cost per gge as a function of electricity cost.