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PEM Electrolyzer Incorporating an Advanced Low-Cost Membrane

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DISCLAIMER

EXECUTIVE SUMMARY

Electrolysis of water, particularly in conjunction with renewable energy sources, is potentially a cost-effective and environmentally friendly method of producing hydrogen at dispersed forecourt sites, such as automotive fueling stations. However, state-of-the-art proton-exchange-membrane (PEM) electrolyzer systems have not been economically competitive for forecourt hydrogen production due to their high capital and operating costs, particularly the cost of the electricity used by the electrolyzer stack.

The forecourt hydrogen application requires an electrolyzer that produces 1500 kg/day (62.5 kg/hr) hydrogen. At the present time, the markets for PEM electrolyzers are for much smaller units, typically less than 5 kg/hr. Although larger stacks have been developed they have not been commercialized. Thus, PEM electrolyzer systems are generally quite small. The primary feedstock for an electrolyzer is electricity, which could be produced by renewable sources such as wind or solar that do not produce carbon dioxide or other greenhouse gas emissions.

In this project, Giner, Inc. (Giner) developed a low-cost, high-efficiency PEM electrolysis stack and system for hydrogen production at moderate pressures of 300 to 400 psig (2170 to 2860 kPa). The electrolyzer stack operates at differential pressure, with hydrogen produced at moderate pressure while oxygen is evolved at near-atmospheric pressure, reducing the cost of the water feed and oxygen handling subsystems. The project included research on catalysts and membranes to improve the efficiency of the electrolysis reaction, as well as development of advanced materials and component fabrication methods to reduce the capital cost of the electrolyzer stack and system. The project culminated in the delivery of a prototype electrolyzer module to the National Renewable Energy Laboratory for testing at the National Wind Technology Center.

Electrolyzer stack efficiency of 74% LHV (87%HHV), meeting DOE 2012 targets, was demonstrated using an advanced high-strength membrane. Giner significantly reduced the capital cost of a PEM electrolyzer stack through development of low-cost components and fabrication methods, including a 60% reduction in stack cost. The estimated cost of the present stack design in large-scale production is less than $350/kW. In addition, Giner demonstrated improved lifetimes of the advanced membrane and cell components that can exceed 60,000 hours of operation. An Economic analysis indicates that hydrogen, prior to delivery costs, could be produced for $3.64 per gge (gasoline-gallon equivalent) at an electricity cost of $0.04/kWh utilizing the lower-cost PEM electrolyzer developed in this project assuming high-volume production of large-scale systems.

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1.0 INTRODUCTION

The Department of Energy (DOE) has identified hydrogen production by electrolysis of water at forecourt stations as a critical technology for transition to the hydrogen economy, and as the hydrogen economy matures, for hydrogen production at centralized locations using renewable energy sources. However, the cost of hydrogen production by present commercially available electrolysis systems is estimated to be \$4.20/kg-H_2 (\$6.60/kg-H_2 dispensed) considerably higher, than the DOE target of ≤\$2.30 (\$4.00/kg-H_2 dispensed) by 2020[1]. Analysis of electrolyzer systems performed by Giner and others using the DOE H2A model indicate that the major cost elements are the cost of electricity and the high capital costs of electrolyzer stacks and systems.

The two major electrolyzer technologies are alkaline and proton-exchange membrane (PEM). Giner Inc. (Giner) developed a differential-pressure PEM electrolysis system. The Giner electrolyzer stack consists of a number of bipolar cells stacked in electrical series, with each cell containing a membrane-electrode assembly (MEA) formed by bonding anode and cathode electrodes to opposing sides of the membrane. The MEA is in contact with electrically conductive anode and cathode support structures located in the oxygen and hydrogen chambers, respectively. An electrically conductive cell separator is located between the anode and cathode chambers of adjacent cells. In the process, high-purity water is pumped to the anode, where it is electrochemically decomposed to oxygen gas, hydrogen ions and electrons. The hydrogen ions move through the PEM and the electrons move through the external circuit to the cathode, where they recombine to form hydrogen. An excess of water is supplied to the oxygen side of the cell and is recirculated to remove waste heat from the MEA. A portion of the excess water is electro-osmotically transported across the PEM with the hydrogen ions. The transported water is separated from the product hydrogen and returned to the water stream.

The Giner PEM electrolyzer technology is much more efficient than the more mature alkaline electrolyzer technology. Giner PEM cells operate efficiently at current densities of 1,500 to 3,000 mA/cm^2, compared to alkaline electrolyzers that typically operate below 300 mA/cm^2. At this current density the alkaline cell voltage is typically 1.9 V or higher. In contrast, the operating cell voltage of the present Giner electrolyzer is lower. In this project Giner demonstrated a PEM electrolysis cell based on an advanced membrane that operates at 1.7 V at 1500 mA/cm^2. Since the cost of electricity is the major contributor to the cost of hydrogen produced by electrolysis, efficient operation is a key to low-cost hydrogen production for large applications. Although the capital cost of PEM electrolyzer stacks is higher than that of alkaline stacks on an area basis, the much higher current density of PEM cells allows the stacks to be 10 times smaller while achieving higher efficiency. Thus, in large-scale production, and with development of lower-cost materials and manufacturing methods for key components, the capital cost of a PEM stack is expected to be competitive with alkaline stacks, while the electricity consumption of the PEM stack will be significantly lower than that of the alkaline stack.

Another key advantage of the Giner PEM technology is the ability to operate the stack at a high differential pressure, allowing hydrogen to be produced at high pressure, while oxygen is produced, and the reactant water is supplied, at near atmospheric pressure. Production of hydrogen in the electrolyzer at elevated pressure provides some systems advantages, decreasing the number of stages of mechanical compression required to store the product hydrogen at greater than 10,000 psig (68.9MPa), the future goal for hydrogen fueling stations.

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[1] The Department of Energy 2012 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan, http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf

However, these advantages must be weighed against the increased capital cost of the higher pressure stack and electrolyzer balance of plant (BOP).

The Giner differential pressure PEM electrolyzer technology is based on the design of the PEM oxygen generating plants (OGP) used onboard the SeaWolf class submarines. Giner manufactured the stack components for six OGP plants. Giner subsequently developed the technology for a 1000-psig (7 MPa) differential-pressure electrolyzer stack. However, the technology is based on the very reliable, but very expensive, electrolyzer stack designs required for submarine applications. The challenge in this DOE project was to modify the differential pressure stack design to significantly reduce stack and system cost, while improving process efficiency, to meet the DOE cost targets for hydrogen production.

2.0 PROJECT OBJECTIVES AND TECHNICAL APPROACH

The primary objective of this project is to develop and demonstrate a cost-effective energy-based system for electrolytic generation of hydrogen. The goal is to increase proton-exchange-membrane (PEM) electrolyzer efficiency and to reduce electrolyzer stack and system capital cost to meet the DOE cost targets for distributed electrolysis. Successful development of the advanced electrolyzer stack and system will result in a high-efficiency, low capital cost electrolyzer that will meet the DOE cost targets for hydrogen production, assuming high-volume production. This will provide competitively priced hydrogen for delivery at forecourt stations to enable transition to a hydrogen economy.

To accomplish this objective, work was conducted by a team consisting of Giner, Inc. (Giner), Virginia Polytechnic Institute & University (VT), and domnick hunter group, a subsidiary of Parker Hannifin (Parker). The project focused on 4 key areas: (1) development of a high-efficiency, high-strength membrane based on perfluorocarbon sulfonic acid (PFSA) or biphenyl sulfone (BPSH) incorporated into a dimensionally stable membrane (DSM) framework; (2) development of a long-life cell-separator; (3) increasing the cell active area to 290 cm^2 (from 160 cm^2), and (4) development of a prototype commercial electrolyzer system. In each of the key development areas Giner and our team members conducted focused development in laboratory-scale hardware, with analytical support as necessary, followed by life-testing of the most promising candidate materials. Selected components were then scaled-up and incorporated into low-cost scaled-up stack hardware developed during this program. The project culminated in the fabrication and testing of a highly efficient electrolyzer system for production of 0.5 kg/hr hydrogen and validation of the stack and system in testing at the National Renewable Energy Laboratory (NREL).

Achievement of high-efficiency operation at high current density required a breakthrough in development of a thin, mechanically strong PEM capable of stable long-term operation at 80 or higher. State-of-the-art PEM electrolyzers use Nafion®[2] 110, 117 or 115 membrane that are manufactured with 1100-equivalent-weight (EW) PFSA and have thicknesses of 0.010″, 0.007″, and 0.005″ respectively. PEM electrolyzers are typically operated at 60°C, with an electricity input of 49.8 kWh/kg, efficiency of 78.9% HHV (66.9% LHV), and cell voltage of 1.85 V at 2000 mA/cm^2 (Nafion 115). Operation at higher temperatures and the use of thinner membranes to achieve higher efficiency is possible in short-term testing, but the strength and durability of Nafion membranes is limited at these conditions.

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[2] Nafion is a registered trademark of E.I. du Pont Nemours and Company

To meet the need for a long-life high-efficiency membrane, Giner developed an advanced dimensionally stable membrane (DSM) that utilized a micro porous support structure imbibed with PFSA. In addition to DSM-PFSA, Giner collaborated with VT to develop a biphenyl sulfone (BPSH) membrane. Both membranes exhibited improved efficiency compared to commercially available membranes. In addition to high-efficiency operation, the DSM-PFSA and BPSH are significantly lower in cost than Nafion membranes in high-volume production. Giner also focused on reducing the amount of the expensive precious metal catalyst required for high-efficiency stack operation through development of higher activity catalysts, improved electrode structures and methods of forming the membrane-electrode assemblies (MEAs).

Giner's approach to decreasing the electrolyzer stack capital cost was to develop lower-cost materials and/or less expensive fabrication methods for the repeating cell components. A major thrust was reducing the parts count/cell, which yielded significant savings in stack assembly labor as well as in stack materials cost. A key finding of the Giner electrolyzer cost studies is that a large cell active area is required to meet the DOE electrolyzer capital cost target. A large cell active area reduces the number of cells required to produce a given amount of hydrogen, and thus reduces the stack manufacturing labor and the materials scrap rate. During this program Giner demonstrated the ability to scale up stack area, by increasing cell area of our legacy design of 160 cm^2 to 290 cm^2. In conjunction with electrolyzer scale-up, Giner also develop a cell separator with improved lifetime in an operating PEM stack, thus reducing stack replacement costs.

Achieving the DOE cost targets also required improvements in the electrolyzer system with respect to capital cost and operating efficiency. In this program Giner teamed with Parker to reduce the cost of the electrolyzer system, primarily through use of low-cost manufacturing techniques of components, and improvements in efficiency of major BOP components such as the hydrogen dryer.

An important objective of this project was to demonstrate and validate high efficiency operation of a low-cost highly efficient PEM-based electrolyzer system. This objective was met by testing a 0.5 kg-H_2/hr electrolyzer module at the National Wind Technology Center (NWTC) at the National Renewable Energy Laboratory (NREL).

3.0 SUMMARY OF ACHIEVEMENTS

The research and development effort in this program was successfully completed. Giner developed a low-cost, high-efficiency proton-exchange membrane (PEM) electrolysis stack and system for hydrogen production at moderate pressure.

High cell efficiency was demonstrated using an advanced high-strength membrane. This membrane enabled the electrolyzer to meet the DOE 2012 efficiency targets. Giner significantly reduced the capital cost of a PEM electrolyzer through development of low-cost components and fabrication methods, including a significant reduction in cell parts count.

A summary of major program achievements is provided below:

- Membrane:
    - Demonstrated Membrane Reproducibility, Durability, and Efficiency
        - Demonstrated high efficiency DSM membranes (single-cell, 5-cell, and 27-cell stacks)
        - Demonstrated 5,000+ hours of scaled-up (290 cm^2) DSM-PFSA membrane at 80°C with estimated lifetime of 45,000 to 55,000 hours
        - Demonstrated high current density (5,000 mA/cm^2) and high pressure (5,000 psig) operation
        - Cell voltage efficiency >87%HHV, 46.6 $kWh_e/kg\text{-}H_2$ (@ 1500 mA/cm^2) meeting 2012 DOE stack efficiency targets
- Cell Separator Development:
    - Demonstrated 5,000+ hrs lifetime of scaled-up cell-separators
    - Demonstrated significantly reduced hydrogen embrittlement with carbon/Ti and other low-cost cell-separators
        - Expected cell-separator lifetime range: 60,000+ hours
- Electrolyzer Stack:
    - Scaled-up stack from 160 cm^2 to 290 cm^2
    - Significant progress made in stack cost-reduction
        - Cell parts count reduced from 41 to 10
        - Utilized low catalyst loadings
        - Stack cost reduced by 60%
    - Stack commercialized & in production: 30-, 60-, and 100-cell configurations
- System Development:
    - Prototype system delivered and evaluated at NREL National Wind Technology Center
        - Stack and system efficiency verified
        - System transferred to NREL's ESIF building (to be used as a demonstrator/learning device)
    - DOE Joule Milestone(s) completed

Utilizing the PEM technology developed during this program, the estimated cost of the PEM stack in large-scale production is less than \$350/kW. A future development path has been identified that would further reduce the capital cost of the stack to <\$300/kW. Economic analysis indicates that hydrogen could be produced for \$3.64/kg-H_2 (production only, no delivery) at an electric cost of \$0.04/kWh by the lower-cost PEM electrolyzer stack and system developed in this project assuming high-volume production of large-scale electrolyzer systems.

This program culminated in the delivery of a prototype electrolyzer module to the National Renewable Energy Laboratory for testing at the National Wind Technology Center. NREL reported an electrolyzer stack efficiency of 74% LHV (87.5% HHV).

4.0 RESULTS AND DISCUSSION

4.1 Membrane

To obtain the required breakthrough in membrane efficiency, development of an advanced thin membrane having high mechanical strength and durability, as well as high protonic conductivity, was required. The membrane development effort employed two approaches that were being developed for proton-exchange-membrane (PEM) fuel cells and extend the approaches to fabrication of membranes for PEM electrolyzers. In the first approach, Giner developed a dimensionally stable-membrane (DSM™) that incorporates perfluorocarbon sulfonic acid (PFSA) ionomer into an engineered plastic micro porous support. The second approach, developed at Virginia Polytechnic Institute & University (VT), utilizes Bi-Phenyl Sulfone (BPSH) hydrocarbon membranes that have high protonic conductivity, excellent mechanical properties and high chemical stability in PEM fuel cells.

4.1.1 DSM™- PFSA Membrane

To improve electrolyzer efficiency, Giner developed an advanced supported membrane having an ionic resistance comparable to that of a 2- to 3.5-mil (0.0020″ to 0.0035″) thick Nafion membrane, but having significantly improved mechanical properties. This advanced membrane is referred to as a dimensionally stable membrane due to the membrane support that minimizes changes in dimensions (swelling/contraction) under high-pressure operation and with changes in water content. The support structure utilized in the development of the DSM consists of a polyimide base film with a definable open pattern. The support structure is then imbibed with PFSA ionomer to a thickness of 3 mils (0.003″). The initial membrane support structures were fabricated using laser micromachining technology. Eventually a more cost-effective technique of fabricating the support structures via chemical-etching was implemented, reducing the cost of the membrane by one order of magnitude.

Laser-drilled DSM supports were fabricated with 30 μm in diameter holes in an 8-μm-thick polyimide support, **Figure 1**. The chemically etched DSM in **Figure 2** is fabricated by etching holes 150 μm (0.006″) in diameter in a 25-μm-thick polyimide film. Although smaller diameter holes (and thinner landings) are more desirable, chemical etching technology with polyimide films is limited to a diameter of 150 μm. The laser-drilled DSM substrates were fabricated with 50% void opening, chemically etch DSM; 60% void opening. The DSM-PFSA MEAs were fabricated by imbibing 700 to 1100 (EW) PFSA ionomer into the DSM support structures.

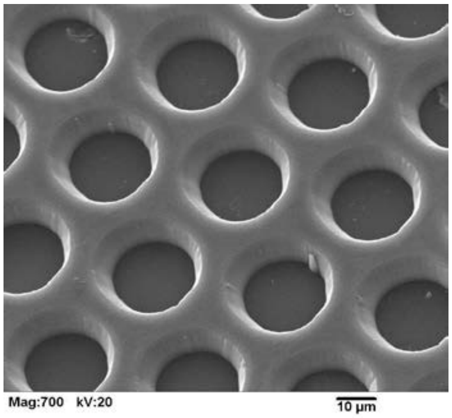

Figure 1. Scanning Electron Microscope (SEM) Micrograph of the Laser-Drilled DSM

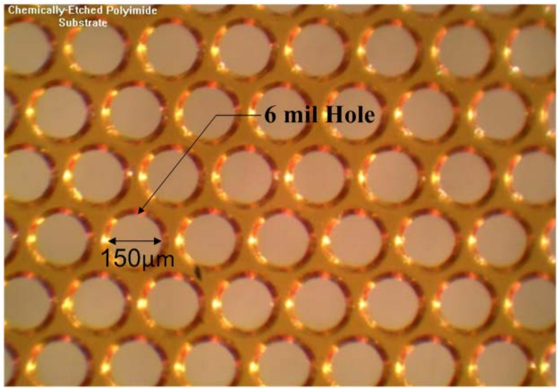

Figure 2. Microscope Micrograph of the Chemically Etched DSM

4.1.2 BPSH Membrane

Bi Phenyl Sulfone (BPSH) membranes have shown to be effective proton exchange membranes under high humidity or liquid water conditions. Testing has shown that their conductivity decreases below 70 or 80% relative humidity (RH), but is not an issue in water electrolysis applications where operation occurs in a flooded state. The hydrophobic-hydrophilic balance of the disulfone functional repeat units of the BPSH co-polymer shown in **Figure 3** determines water uptake, conductivity, and mechanical behavior. Virginia Polytechnic Institute & University (VT) prepared several BPSH samples that ranged from 35 to 50% of the disulfone functional repeat units.

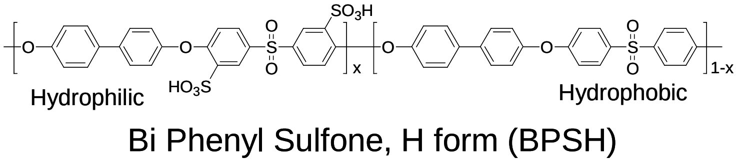

Figure 3. BPSH Membrane

For each BPSH membrane, conductivity and ion-exchange-capacity (IEC) measurements at a temperature of 80-90°C and 100% RH (simulating electrolyzer conditions) were measured. BPSH membranes with 35 and 40% disulfone (BPSH-35 & BPSH-40) exhibited the necessary properties for high cell performance and were selected for further evaluation. Membrane conductivity along with the respective IEC values is shown in **Table 1**. In addition, the BPSH-35 membrane demonstrated the highest degree of dimensional stability during water uptake measurements, **Figure 4**. Compared to a 2 mil (0.002″) thick Nafion (112) membrane , the BPSH-35 membrane exhibited one half the mass increases.

Table 1. BPSH Membranes

Sample	Conductivity (S/cm)	IEC (meq/g)	Thickness (microns)
BPSH-35	0.127	1.53	37
BPSH-40	0.200	1.72	35
Nafion 112	0.203	0.91	50

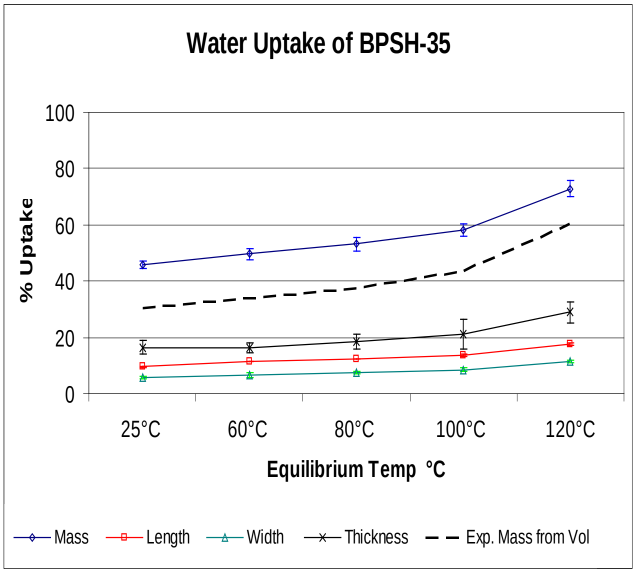

Figure 4. Dimensional Measurement of BPSH-35 Membrane

A significant advantage of the BPSH membrane, compared to Nafion, is its low gas permeation rates. A major goal of the BPSH membrane development effort was to increase the ratio of membrane conductivity vs. hydrogen (H_2) permeability. The importance of increasing the ratio of conductivity vs. permeability can be seen in cell efficiency. Depending on this ratio, membranes with good conductivity and a low gas permeation rate can be made very thin. Thinner membranes exhibit lower cell resistance and higher electrolyzer cell efficiencies. The conductivity/permeability ratio of BPSH-35 is a 5 x improvement over that of Nafion 1100 EW membrane. **Figure 5** depicts simulated electrolyzer performance at 80°C and 1000 psi for Nafion 1100 EW and BPSH-35 membranes. A considerable advantage in electrolyzer performance or cell energy consumption (kWh/kg-H_2) is seen by raising this ratio. The expected performance increase was confirmed in testing of the BPSH membrane in an operating electrolyzer (*section 4.1.3*).

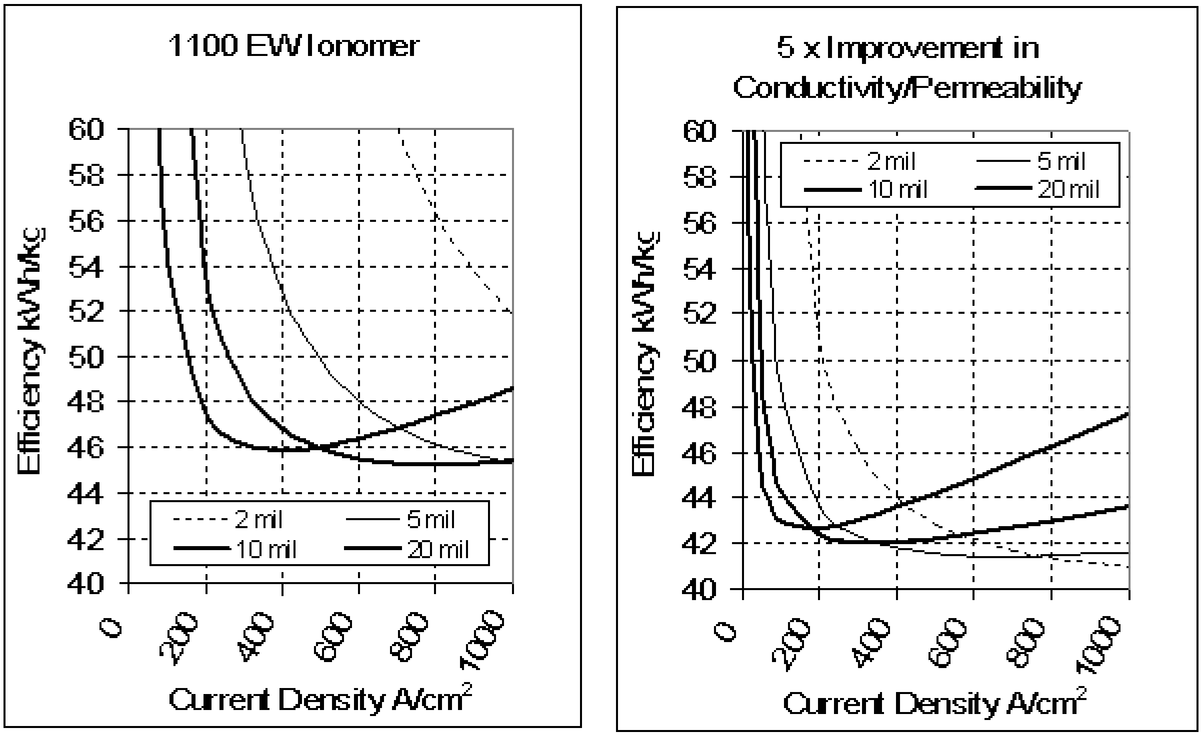

Figure 5. Simulated Electrolyzer Performance

The H_2 gas permeability of BPSH-35, tested at various temperatures and humidity, compared to Nafion membrane at 80°C is shown in **Figure 6.** The data is correlated in terms of pressure, time, and membrane thickness and reported in terms of Gas Transmission Rate (GTR) in units of mol-H_2/KPa.s.cm. Results indicate that the H_2 permeation through BPSH-35 is 1/10 that of Nafion membrane of similar thickness and is suitable for use in differential pressure PEM electrolyzers.

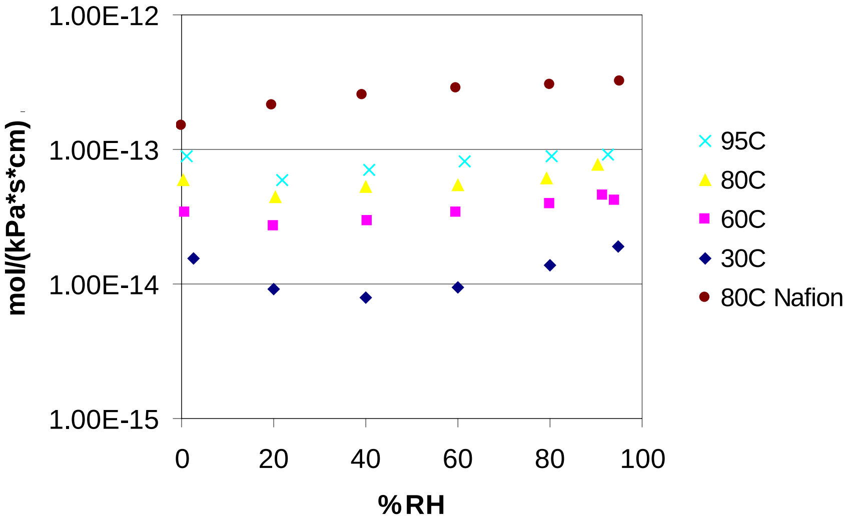

Figure 6. H_2 Permeation of BPSH-35

The BPSH-35 (and -40) membranes exhibited low hydrogen gas permeability, low-water uptake (swelling), IEC values higher than that of Nafion, and acceptable conductivities. These membranes were fabricated into membrane-electrode-assemblies (MEAs) and evaluated in single-cell electrolyzer hardware.

4.1.3 Membrane Performance

Polarization scans of the DSM-PFSA and BPSH MEAs were conducted through a current density range of 250 to 3000 mA/cm², and a temperature of 80°C in single-cell hardware. All MEAs had similar cathode and anode electrode structures. Results were compared to commercially available Nafion MEAs typically used in PEM electrolysis, **Figure 7**.

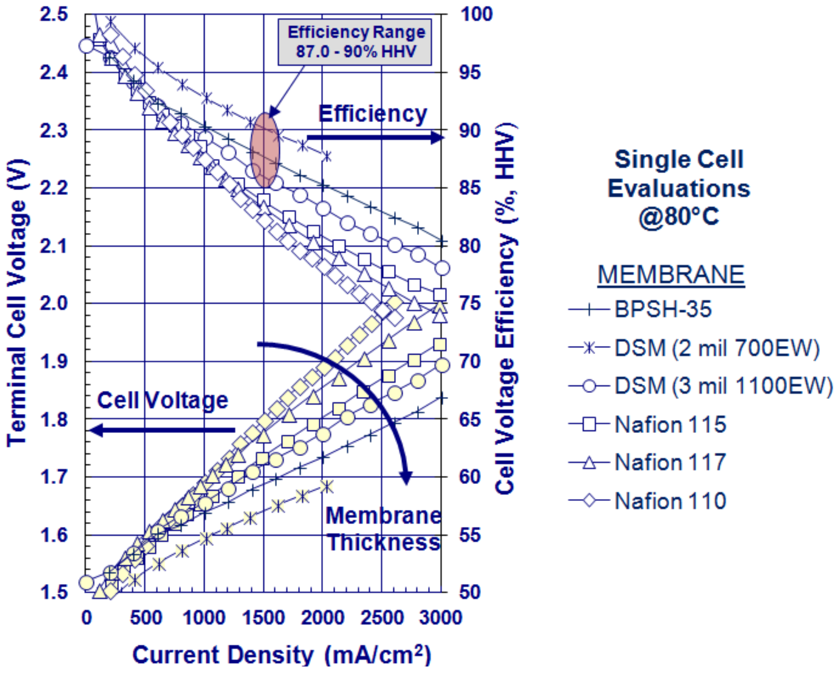

Figure 7. Performance Comparison of DSM-PFSA & BPSH vs. Nafion Membranes

All DSM-PFSA and BPSH MEAs that were fabricated and evaluated in the PEM electrolysis stack hardware met the criterion for performance: each of the MEAs exhibited lower cell voltages and thus higher cell efficiencies than that of state of the art Nafion membranes currently used in PEM electrolysis. In separate testing, direct comparison of the **chemically** etched DSM-PFSA and **laser-drilled** DSM-PFSA (both imbibed with 1100EW) indicates a small reduction in performance from 1.72 V (laser-drilled DSM-PFSA) to 1.75 V (chemically etched DSM-PFSA) at a current density of 1500 mA/cm². This is a result of the larger landing width of the **chemically** etched DSM. Larger landing widths increase the proton transport path restricting transport kinetics.

The BPSH-35 and DSM-PFSA membranes fabricated with low equivalent weight ionomers (700EW) exhibited the lowest cell voltage (highest cell performance). The BPSH-35 MEA exhibited a cell performance equivalent to or better than that of a Nafion membrane with an equivalent thickness of 2 mil (0.002″). Although the conductivity of Nafion 1100EW is twice that of BPSH-35, the 1.4 mil (0.0014") thick BPSH-35 membrane outperforms Nafion of similar thickness and has a H_2 gas permeation rate equivalent to a 10 mil (0.010″) Nafion membrane. Based on these results, the BPSH-35 membranes were selected as candidates for 1000-hour durability life testing.

4.1.4 Membrane Durability Testing

A critical factor for stack lifetime is chemical and mechanical durability of the membrane, especially when thin membranes are used in high-performance stacks. To demonstrate reproducibility and durability, 1000-hour life testing of the DSM-PFSA and BPSH MEAs were conducted in an operating electrolyzer stack having an active area of 160-cm². Select MEAs were then scaled up to 290 cm² and evaluated in a 5-cell scaled-up electrolyzer stack for a similar period of time. Testing was performed at an operating current density of 1500 – 1750 mA/cm², at an elevated operating temperature of 80°C, and a differential pressure of 300 psi to simulate actual operating conditions in the electrolyzer system.

4.1.4.1 DSM-PFSA Membrane Durability

The chemically etched DSM MEAs were selected for life testing due to ease of manufacturing and reduced fabrication costs. During the 1000-hour life test of the DSM-PFSA, the performance and durability of the membrane was assessed by two major characterizations: fluoride release rate (FRR) and voltage performance. PFSA membranes contain a large amount of fluorine (>65%). When the membrane is chemically degraded, HF is usually the most abundant product. Since PFSA is used as the membrane material and in the binder for the catalyst layer, FRR can be used as the measurement for membrane chemical degradation. Giner has developed extensive experience in characterizing membrane chemical degradation by FRR. Based on the FRR results, the lifetime of the MEA can be projected. Generally, 10% total fluoride inventory loss is considered as the end of life for MEAs.

During 1000-hour life testing of a single-cell 160 cm² DSM-PFSA MEA, low FFR and high cell efficiencies were observed. The DSM-PFSA MEAs were then scaled up to 290 cm² and a 5-cell stack was assembled and evaluated for 1000 hours. At the completion of the 1000-hour life test, the stack was disassembled to evaluate the membrane and cell components. A single MEA from the 5-cell stack was re-assembled as a single-cell stack. Life-testing was resumed on the single-cell DSM-PFSA MEA while cycling the operating current density between 1500 mA/cm² (435A) to 1750 mA/cm² (507A), **Figure 8**. The re-use of the MEA from the disassembled 5-cell stack resulted in an increase in contact resistance and a slight increase in cell-voltage after reassembly (@ ~1090-hour mark). The DSM-PFSA MEA was then operated successfully for an additional ~4430 hours, with no additional voltage degradation. The DSM-PFSA MEA was operated for a total of 5430 hours.

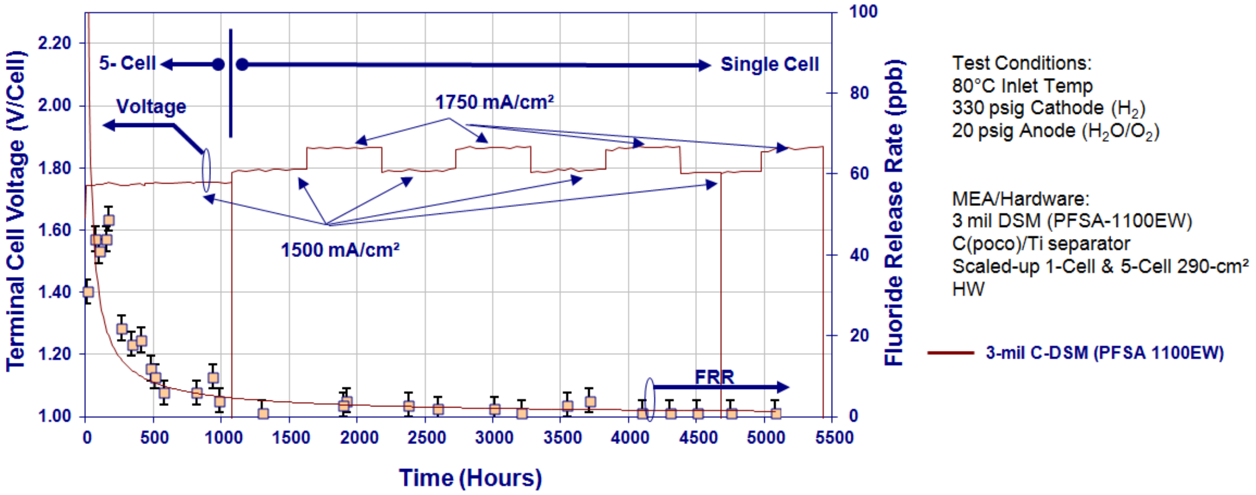

Figure 8. 5000+ Hour Life Test of a DSM-PFSA MEA

When removing MEAs from assembled cells, impressions from the cathode and anode support materials remain on the MEA surface. This results in reduced contact and an increase in cell resistance after reassembly. This was evident as shown by the slight decrease in performance immediately after the single-cell was reassembled. Although the cell efficiency remained high after reassembly, a voltage increase of 50 mV was observed. A “performance recovery” is characteristic after a cell has been reassembled. This occurs as the MEA reshapes and contact to the support materials is increased. However, this was not observed due to the nature of the “dimensionally stable” membranes (DSM) in which there is little to no membrane movement. This suggests that DSM MEAs can be removed & reused but a voltage penalty may be incurred.

Based on fluoride loss data obtained during the 5,000+ hour DSM-PFSA life-test, an average fluoride release rate of less than 4 ppb was measured. Taking into account that the FFR measurement is an average measurement, testing conducted at an elevated operating temperature of 80°C, and the membrane has a thickness of 3 mil, and failure occurs when 10% of the membrane fluoride is lost, the **DSM-PFSA MEA estimated lifetime is estimated to be between 45,000 and 55,000 hours**, which exceeds the durability requirements of this program. Following the completion of the 5,000+ hour life-test, the stack was dissembled to investigate hydrogen embrittlement within the cell-separator and stack components (*section on 4.2.1*). Based on cell performance and membrane durability, the DSM-PFSA MEAs were selected for use in the full-scale final stack assembly.

4.1.4.1.1 DSM-PFSA Membrane Durability at High Current Density & Pressure

The membrane and stack components developed during this program are designed to operate at significantly higher current densities than those in typical PEM-based electrolyzers by a factor of 3x. The high efficiency of the membrane, at high operating current density, provides a cost advantage by enabling the use of off-peak renewable power, such as wind energy, when electrical demand (and electrical costs) is low.

The life of an ion-exchange membrane can vary from a few hours to 10’s of thousands of hours. It is clear from fluoride-release-rate (FRR) studies of PEM-based electrolyzers (and fuel cells) that the H_2/O_2 environment and catalytic electrodes bonded to the membrane represent a harsh atmosphere that contributes to the membrane degradation. Aggressive operating conditions such as elevated temperature, pressure, and current density, can also accelerate membrane degradation. The degradation mechanism is related to the formation of a peroxyl species that occurs within the membrane when H_2 and O_2 interact[3]. The peroxide radicals attack and breakdown the fluorocarbon backbone in perfluorosulfonic acid (PFSA) membranes. Although advancements by manufacturers have been made to stabilize PFSA ionomers, the absence of peroxide radicals in the PEM can lead to considerably less membrane degradation.

To mitigate the effect of membrane degradation, Giner advanced the DSM membrane formulations via the addition of proprietary additives that mitigate degradation by breaking down the peroxide radicals, yet maintain membrane cell performance. To demonstrate this, Giner assembled a 5-cell stack, utilizing an 'Advanced DSM-PFSA' membrane imbibed with proprietary additives. The Advanced DSM was operated for a period of 1,000 hours at an elevated current density of 5,000 mA/cm². The data was compared to non-treated DSM-PFSA membrane that had been tested at a current density of 1,500 and 5,000 mA/cm² for a similar period of time. In all tests, the temperature and pressure were maintained at 80°C and 330 psig, respectively.

The average FRR obtained after the 1,000-hour life-test of a standard (non-treated) DSM-PFSA membrane, operating at a current density of 1500 and 5000 mA/cm² indicate that the amount of fluoride loss is the same per unit of current passed through the membrane. This indicates that a membrane operating at 3x the nominal current density will have 1/3 of the life expectancy. As determined previously, the expected lifetime of non-treated DSM-PFSA membrane, operating at a nominal current density of 1,500 mA/cm², is 45,000 to 55,000 hours. At a current density of 5,000 mA/cm² the lifetime is reduced to 10,000 to 12,000 hours. However, the Advanced DSM-PFSA fabricated with the additives indicates a life time of >40,000 hours at 5,000 mA/cm² under similar operating conditions. Voltage performance measured during testing indicated no loss in cell voltage, **Figure 9**.

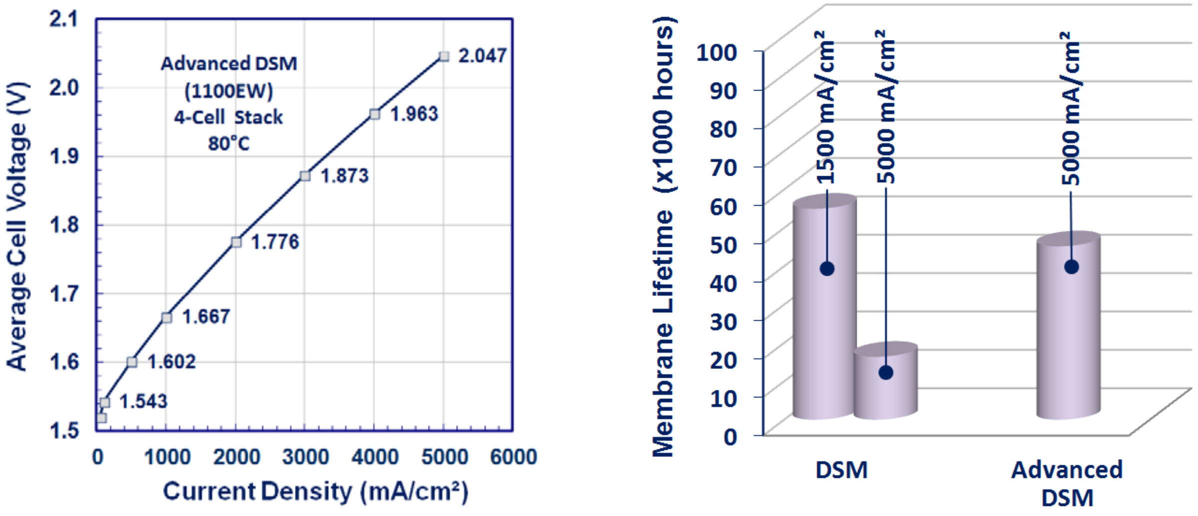

Figure 9. Fluoride Release Rate (FRR) Comparison

Based on this result, the '**Advanced DSM' membrane, operating at the nominal current density of 1,500 mA/cm², is estimated to operate for approximately 200,000 hours**. Further evaluations are required to determine if the additive remains in the membrane after extended

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[3] LaConti, A. B., Hamdan, M., McDonald, R. C. (2010). Mechanisms of membrane degradation. Handbook of Fuel Cells, John Wiley & Sons, Ltd.

operation, however it is clear that the Advanced DSM-PFSA membranes have the potential of reducing operating and maintenance (O&M) costs related to membrane replacement in PEM-based electrolyzer systems.

In addition to high-current-density operation, the DSM membranes were evaluated at an elevated pressure of 5,000 psig to determine mechanical durability. Four DSM-PFSA membranes were placed in high-pressure electrolyzer stack hardware[4] and evaluated at up to 80°C. The DSM membrane used in this test was engineered to accommodate high-pressure operation and low gas permeation and were fabricated with a thickness of 7 mils (0.007″). The membranes were compared to Nafion 110, a 10-mil (0.010″) thick 1100-equivalent-weight (EW) membrane, tested in the same hardware under similar operating conditions.

The hydrolytic properties of PFSA membranes, which include the family of 1100EW Nafion membranes (N115, N117, and N110), have linear expansions of 15% and thickness changes of 14% when hydrated[5]. Furthermore, as a result of the high clamping forces that are required to seal against the membrane surface while operating at high pressure, an additional dimensional change occurs due to the extrusion of the PFSA ionomer. The Nafion 110 film tested at 5,000 psi extruded into the fluid ports (and overboard) of the cell-frame. This presents sealing and performance issues after short durations of operation (<100 hours) that eventually limit the lifetime of the electrolyzer stack. In contrast, the DSM-PFSA membranes developed during this program remain dimensionally stable at high operating pressures and under high clamping forces. Only a 1% dimension change was observed in the sealing area with DSM-PFS MEAs.

The Giner DSM membrane advantages demonstrated are:

- **High strength, High efficiency**
- **No x-y dimensional changes upon wet/dry or freeze-thaw cycling**
- **Customized MEAs to provide more support at edge regions and/or at ports**

4.1.4.2 BPSH Membrane Durability

Life-testing was also conducted on the BPSH-35/40 membranes under similar operating conditions. During the 1,000-hour life-test, hydrogen crossover (from cathode to anode compartment) was detected and testing was automatically suspended. Given that cross-cell leakage was not observed during ambient pressure and temperature testing, the initial assumption was that the hydrogen crossover may have occurred due to the inability to seal the thin BPSH membranes against the electrolyzer cell-frames at pressurized operation. However similar results (cross-cell leakage) were obtained with BPSH membranes assembled in hardware with specifically modified cell-frames for use with thin membranes. During membrane analysis, it was determined that the lower than expected lifetime was the result of chemical degradation related to the formation of a peroxyl species that occurs within the membrane. The peroxide radicals attack and breakdown the hydrocarbon backbone of the BPSH polymer. Although the BPSH membrane lifetimes were eventually improved via the addition of an additive that mitigates peroxide radical formation, the DSM-PFSA membrane was selected for use in the final stack assembly due to improved lifetimes. Additionally, the additives that were developed for the BPSH membranes were also used to enhance the DSM-PFSA lifetime as demonstrated under high current density operation as noted earlier in section **4.1.4.1.1**.

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[4] Stack hardware developed under DOE program DE-SC0001486, Unitized Design for Home Refueling Appliance for Hydrogen Generation to 5,000 psi

[5] Properties of Nafion PFSA Membrane, http://www2.dupont.com/FuelCells/en_US/assets/downloads/dfc101.pdf

4.1.5 Catalyst Loadings

A variety of alternative electrode preparation methods that potentially offer improvements in electrolyzer cost and performance were investigated. The primary thrust of this area was to study alternative coating and printing methods that produce better electrode decals with more efficient use of materials. In particular, this broad-ranging study looked at both dry and wet printing/coating methods for improved catalyst coverage of the MEA, reduced catalyst losses during the preparation of electrode decals, and/or reduce or eliminate the use of organic solvents in the decal preparation process. This resulted in the fabrication of MEAs with a total platinum (Pt) catalyst loading of 1 mg-Pt/cm² (anode and cathode). As a comparison, Giner's legacy MEAs utilized a catalyst loading equivalent to 4 mg-Pt/cm² on both the anode and cathode (8 mg-Pt/cm² total). Both the DSM-PFSA and BPSH MEAs fabricated during this program utilized the low-loaded catalyst structures during performance and life test evaluations. MEAs developed for the full scale electrolyzer stack also utilized this low-loaded catalyst.

In separate testing, Giner investigated the performance of 3M's nanostructured thin film (NSTF) catalyst alloys of $Pt_{68}Co_{29}Mn_3$, $Pt_{50}Ir_{50}$ and $Pt_{50}Ir_{25}Ru_{25}$, with Pt loadings in the range of 0.1 to 0.2 mg/cm^2, for use in PEM-electrolyzers[6]. The Pt loading of 3M's NSTF catalyst is nearly one order of magnitude lower than that developed by Giner (1.0 mg-Pt/cm²). In cooperation with 3M, Giner delivered Nafion N117 membranes to 3M. 3M used the N117 to fabricate several ½CCM (MEAs with catalyst on the cathode side of the membrane only for evaluation in an operating electrolyzer. Since the cathode catalyst was designated for evaluation, a 4 mg/cm² Pt-Ir catalyst was used on the anode side of the MEA in order to minimize any anode performance losses. The size of the MEAs delivered to and evaluated at Giner were ~4″ x 4″. Each MEA was evaluated in Giner's evaluation-hardware which consisted of an active area of 50 cm². Performance was compared to a standard Nafion 117 MEA fabricated with a cathode electrode having a Pt loading of 4 mg/cm², **Figure 10**.

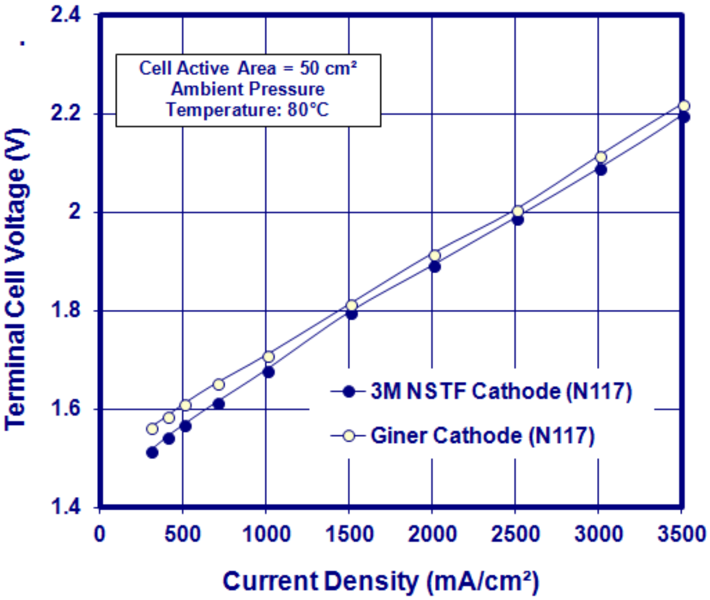

Figure 10. 3M vs. Standard Pt Catalyst

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[6] J. Electrochem. Soc. 2012 volume 159, issue 6, K165-K176 Initial Performance and Durability of Ultra-Low Loaded NSTF Electrodes for PEM Electrolyzers",M. K. Debe , S. M. Hendricks, G. D. Vernstrom, M. Meyers, M. Brostrom, M. Stephens, Q. Chan, J. Willey, M. Hamdan, C. K. Mittelsteadt, C. B. Capuano, K. E. Ayers, and E. B. Anderson [7] NREL, H2A Central Hydrogen Production Model, Version 3 User Guide (DRAFT),D. Steward, T. Ramsden, J. Zuboy

As shown in Figure 10, 3M's low-loaded cathode catalyst slightly outperforms an MEA with a 4 mgPt/cm² cathode catalyst through a current density range of 3,500 mA/cm². A "blinding effect", that occurs when thicker catalyst loadings are used due to the loss of active sites when hydrogen gas bubbles migrate through the catalyst layers, is minimized with the thin film (or low loaded electrodes) of 3M's NSTF catalyst.

Equivalent cell performance was shown utilizing Giner's and 3M's low loaded catalyst structures. Giner developed catalyst structures that reduced the Pt loading from 8 to 1 mg/cm² and were successfully utilized in the fabrication of DSM-PFSA and BPSH MEAs. In addition, 3M's NSTF cathode catalyst, containing 0.1 to 0.20 mg-Pt/cm² per electrode, exhibited a performance equivalent to heavier cathode catalyst of 4 mg/cm² in PEM-based electrolyzer applications.

4.2 Scaled-up Stack Development

4.2.1 High-Durability Cell Separator

The cell separator is a gas-impermeable conductive sheet that separates the hydrogen and oxygen compartments in adjacent cells. In addition to being highly conductive, the cell separator must be resistant to hydrogen embrittlement and to corrosion in an oxidizing environment. The proven Giner electrolyzer designs use a complex multi-layer separator incorporating a conductive compliant member between a sheet of niobium on the oxygen side and a sheet of zirconium on the hydrogen side. This design is very durable, but is very expensive, both due to the costly valve metals and to labor-intensive fabrication.

In this program Giner proposed to develop a low-cost cell separator that is projected to have an operating lifetime greater than 10,000 hours, with a goal of achieving 40,000 hours with further development. Giner investigated two approaches: (1) a two-layer structure consisting of Zr deposited on titanium (Ti) foil (Zr/Ti and ZrN/Ti); and (2) a gas-impermeable conductive carbon plate having a Ti foil protective layer on the anode side (carbon/Ti). Separate testing was also conducted on cell separators developed by outside vendors and included cell separators from TreadStone that utilized their patented 'microdot' technology.

Several designs of the carbon/Ti, Zr/Ti, and ZrN/Ti were fabricated with an active area of 160 cm². The carbon in the carbon/Ti cell separator was fabricated using Pyrolitic graphite (POCO) from Entegris Corporation. This cell separator consisted of a 30-mil (0.030″) thick POCO carbon disc bonded onto a Ti substrate. In addition, the POCO carbon is surface sealed to ensure that hydrogen does not permeate through the carbon layer and contact the Ti substrate. The Zr/Ti and ZrN/Ti cell separators were fabricated by depositing a 5-μ layer of Zr or ZrN onto the Ti substrate via physical vapor deposition. All cell-separators met the criterion for conductivity; >300 S/cm. Hydrogen embrittlement studies were conducted on each of the samples after 500 hours of testing in an operating electrolyzer stack to determine if further scale-up to 290 cm² would be valid.

At the completion of each of the 500-hour life tests, the stacks were disassembled and coatings were visually inspected to determine degradation. Visual inspection of the Zr/Ti and ZrN/Ti cell separators revealed a loss of the Zr and ZrN coatings. This was also evident from the analysis of the electrolyzer anode water. During operation the water quality (resistivity) dropped from 15 to 1.5 MΩ-cm indicating a contaminate had entered the anolyte. No contamination or degradation of the carbon/Ti cell-separator was observed. Water quality of the carbon/Ti cell separator after 500 hours of operation was measure at 14.7 MΩ-cm.

Hot vacuum extraction was used to determine hydrogen uptake within the Ti substrates at the end of the 500-hour evaluation. This is a destructive test in which various sections of the Ti component of the cell separators are examined for hydrogen content. Life time estimates can be made based on the amount of absorbed hydrogen within the Ti. Hydrogen embrittlement occurs by two methods, (1) atomic hydrogen absorbed on the Ti surface migrates into the metal lattice and recombines to form molecular hydrogen. When the pressure of the molecular hydrogen exceeds the strength of the metal cracking will occur, and (2) absorbed hydrogen can form a titanium hydride. The rate of absorption is dependent on several factors including operating temperature & pressure. Thus all separators were evaluated in an operating electrolyzer under the operating conditions of the electrolyzer system (80°C and 300 psid) prior to analysis. Although hydrogen embrittlement data is not readily available for PEM-based electrolyzer components, extensive testing at Giner indicates that the cell separator will fail when hydrogen uptake exceeds 0.8% by weight.

Based on the hydrogen uptake results of the 500-hour life testing, the carbon/Ti, Zr/Ti, and ZrN/Ti estimated life-times would exceed the 40,000-hour bench mark assuming a linear hydrogen uptake value over the entire life of the separator (although this may not be the case for Zr/Ti and ZrN/Ti due to the coating loss). It should also be noted that the hydrogen uptake value for ZrN/Ti was lower than that of the titanium control sample (titanium as received from the vendor). During the PVD deposition of ZrN and Zr on titanium, the samples are heated at high temperatures releasing an unknown amount of absorbed hydrogen. As a result of the cell separator performance, the carbon/Ti cell separator was selected for scale-up to 290 cm², **Figure 11**.

Figure 11. 290 cm² Carbon/Ti Cell-Separator

Testing of the scaled-up 290 cm² carbon/Ti cell-separators was conducted in the scaled-up electrolyzer stack hardware while simultaneously evaluating the membrane durability (**see section 4.1.4**). Testing was conducted over a period of 5430 hours. A comparison of the hydrogen uptake values for each of the cell-separators is shown in **Table 2**.

Table 2. Results and Comparison of Cell-Separator Materials

Cell Separator Material	Active Area (cm²)	Time (Hours)	H_2 uptake (ppm)
Carbon/Ti	**290**	**5430**	**104**
Zr/Ti	160	500	140
ZrN/Ti	160	500	31
Dual Layer Ti	160	500	1105
Ti (baseline un-tested)	160	0	≈ 60
All cell-separators tested in PEM electrolyzer stack at 1500-1750 mA/cm² and 80°C. Titanium Failure (Embrittlement) occurs at ~8000 ppm			

The most promising approach for long-term implementation was observed by coating titanium with a low-cost electrically conductive, embrittlement-resistant carbon coating. The challenge was the development of a pinhole-free, highly adherent coating with the required characteristics. Under the cell-separator development task, Giner demonstrated performance of a carbon/Ti cell separator in scaled-up 290-cm² electrolyzer stack hardware. Performance is comparable to that of the legacy niobium-zirconium separator. In addition, **life expectancy of the carbon/Ti cell separator, determined via hydrogen-uptake analysis over a 5,000-hour period, indicates lifetimes exceeding 60,000 hours.** In addition, separate testing was conducted on cell separators developed by outside vendors. This included cell separators fabricated using an alternative low-cost carbon on titanium, a nitrided titanium cell-separator, and a titanium cell separator developed by TreadStone that utilized a protective oxide coating with gold and platinum microdots as current-carriers. Testing indicated that high cell separator performance was obtained using the TreadStone coating. This separator indicated lifetime similar to or better than that of the carbon/Ti and had a hydrogen uptake measurement of only 55 ppm after 5,300+ hours of testing.

4.2.2 Electrolyzer Stack

Forecourt hydrogen applications require an electrolyzer system that produces 1500 kg/day (62.5 kg/hr) hydrogen. At present, the markets for PEM electrolyzers are for much smaller units, typically less than 5 kg/hr. Although larger stacks have been developed they have not been commercialized. Thus, PEM electrolyzer stacks are generally quite small. Utilizing stacks with an active area of 160 cm², the forecourt hydrogen station would require approximately 40 stacks, each having 100 cells. It may be possible to increase the number of cells per stack, but a large number of stacks would be required.

For cost-effective production, as well as to minimize system footprint and maintenance, the stack active area must be scaled-up to as large an area as is practical. In commercial chlor-alkali production, the largest cells are the most cost effective; however, chlor-alkali cells operate at near atmospheric pressure, whereas operation at 300 psig is proposed for hydrogen production. Eventual scale-up of the 300 psig PEM electrolyzer to an active area of 0.2 m^2 or greater seems feasible. This would reduce the number of stacks required for the forecourt application to 5 stacks of approximately 100 cells each, operating at a current density of 1800 mA/cm^2.

Scale-up of this magnitude is beyond the scope of this project. However, to demonstrate the ability to scale-up a moderate pressure electrolyzer design, Giner designed and fabricated a stack having an active area of 290 cm^2. The stack was redesigned to incorporate the low-cost components and cell-separators designed in this program.

The electrolyzer stack costs are the main driver of electrolyzer system costs. Even in prototype quantities, stack costs (materials and assembly labor) are approximately two-thirds of the total system cost. The electrolyzer stack is made up of many cells (repeating units) and a set of compression hardware which include the end plate(s), tension rods, bolts (also known as the non-repeating hardware), see **Figure 12.**

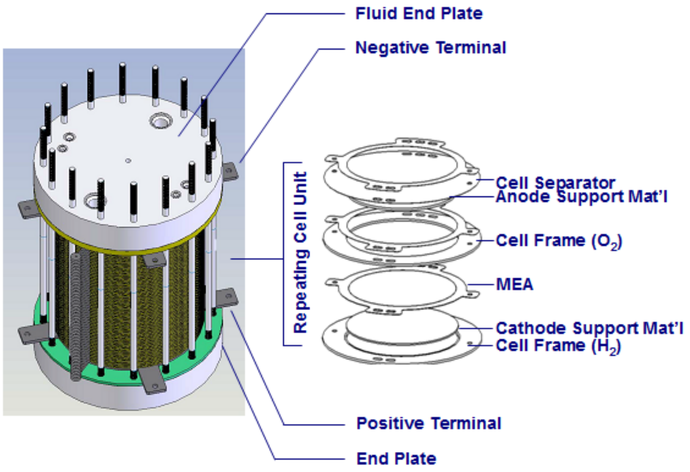


Figure 12. Stack Assembly

For large-scale stacks of the kind under discussion here, the repeating unit cost accounts for approximately 90% of the total stack cost. In addition to scaling-up the MEAs and cell-separators, the remaining stack components including the cell-frames, anode and cathode support materials, endplates, and other miscellaneous components, also required scale-up. Thus the opportunity was taken to redesign the remaining stack components to reduce costs. A summary of cost reduction measures implemented during this program are noted below:

1. In addition to molding the 290-cm^2 scaled-up cell-frames (a 95% cost-reduction over machining), the thickness of the cell frames has been reduced by 30% (from 0.100″ to 0.066″ thick). This reduces the thickness of the anode and cathode-side-support-materials (located inside the frames) by 30% and consequently the material cost by 30%. This new thin-frame was used during the 5-cell short-stack life-test and was incorporated into the deliverable stack.
2. The repeating part count per cell has been reduced to 10 (originally 41 parts/cell at the start of this program, and 16 parts/cell in 2009); the result is a reduction in labor costs by over 50%.
3. The electrolyzer stack was fabricated with low-cost alternative materials developed in this program. The alternative materials replace expensive valve metals. This includes the cell-separator developed in this program, but more recently the anode and cathode support materials within the cell-frames. The material cost reduction is up to 98% lower when replacing niobium; 75% lower when replacing zirconium.
4. The electrolyzer stack end plate has been fabricated with carbon steel vs. stainless steel; material cost of the endplate has been reduced by 60% (this is not a repeating unit, but does further reduce the cost of the electrolyzer).

As a result of stack component and membrane development during this program, and in addition to reduction in cell-part counts, the overall projected capital cost of the electrolyzer stack has decreased from greater than $1000/kW in 2007 to <$350/kW in 2013 for large scale manufacturing of up 1500MW/year, (Figure 13). In addition, the electrolyzer stack developed during this program was commercialized and is currently available in 30-, 60-, and 100-cell configurations.

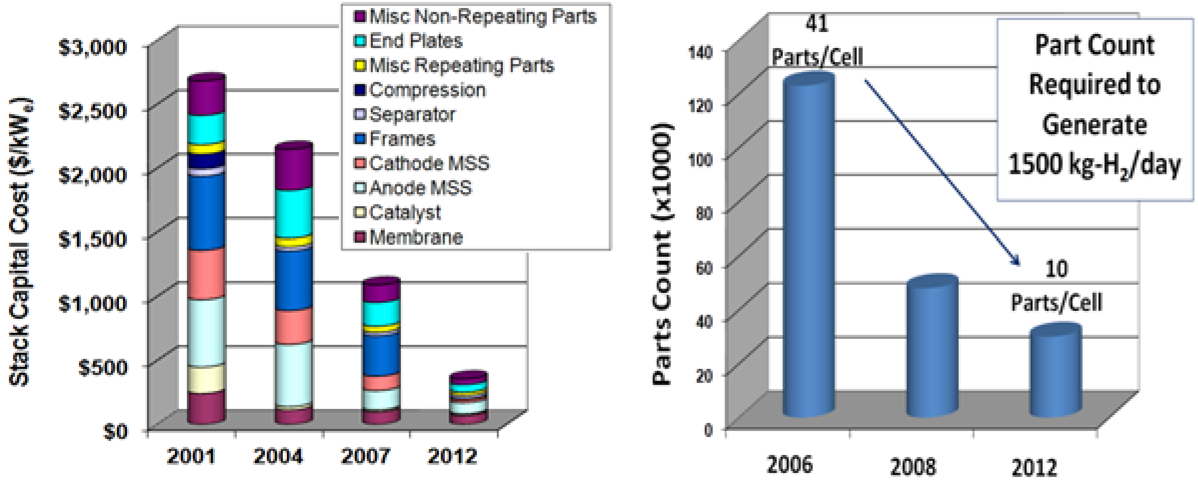
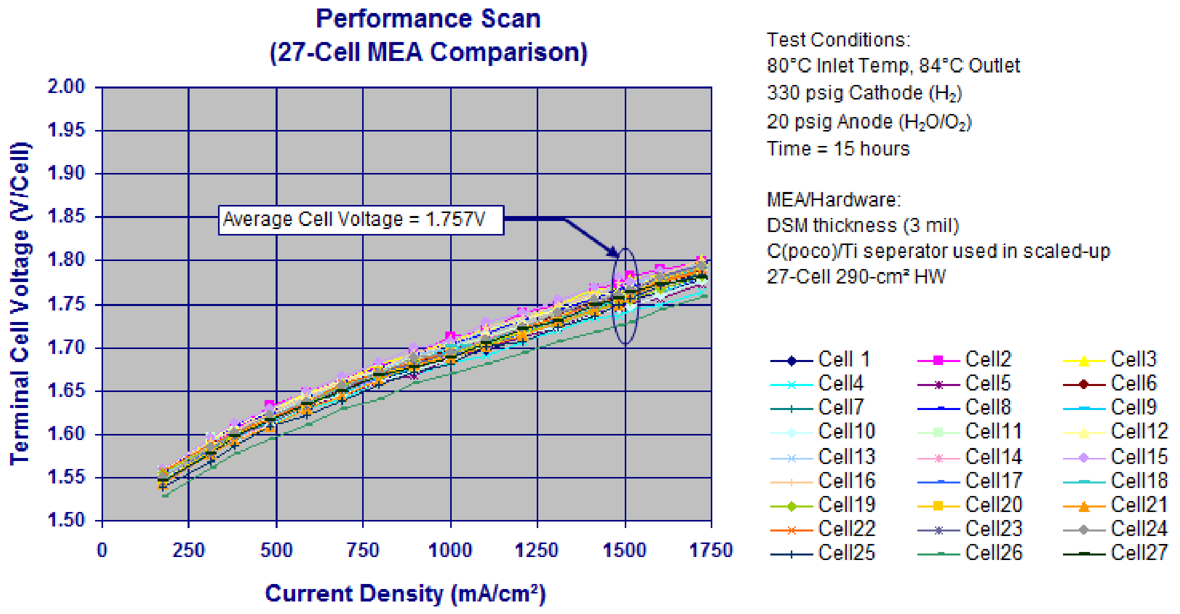


Figure 13. Stack Advancements and Cost Reductions

4.3 Electrolyzer Stack

A 27-cell stack, producing 0.5 kg-H$_2$/hr, was assembled using the DSM-PFSA membranes and scaled-up stack components developed during this program. Polarization scans were conducted every 5 hours to compare short term performance. The DSM-PFSA MEAs exhibited continued improvement as the MEAs gradually hydrated during operation. A variance of 30 mV between the lowest and highest cell voltages was measured at low current density operation (250 mA/cm²); 50 mV, at the highest current density operation (1750 mA/cm²), **Figure 14**. Cell voltages converged over the operating current density range as MEA hydration improved. Polarization scans indicated that the average cell performance in the 27-cell electrolyzer stack is comparable to that of a 3.5-mil (0.0035″) thick Nafion membrane at current densities of 1500 mA/cm². An average cell efficiency (up to 87.5% HHV), operating in the cell voltage range of 1.757 V/cell at a current density of 1500 mA/cm² was measured.



Test Conditions:
80°C Inlet Temp, 84°C Outlet
330 psig Cathode (H$_2$)
20 psig Anode (H$_2$O/O$_2$)
Time = 15 hours

MEA/Hardware:
DSM thickness (3 mil)
C(poco)/Ti seperator used in scaled-up
27-Cell 290-cm² HW

Figure 14. MEA Comparison in 27-Cell Stack

In an electrolyzer system, the stack is operated at constant current. The heat generated from the electrolyzer stack is used to heat the water reservoir until the water temperature is at 80°C. As the electrolyzer stack warms up additional current is applied to the stack at constant voltage. In order to simulate actual operating conditions in the system, a constant voltage verses temperature scan was conducted. At an inlet temperature of 81°C the stack operating performance goal of 1.755 V/cell at 1500 mA/cm² is achieved (87% HHV efficiency), **Figure 15**.

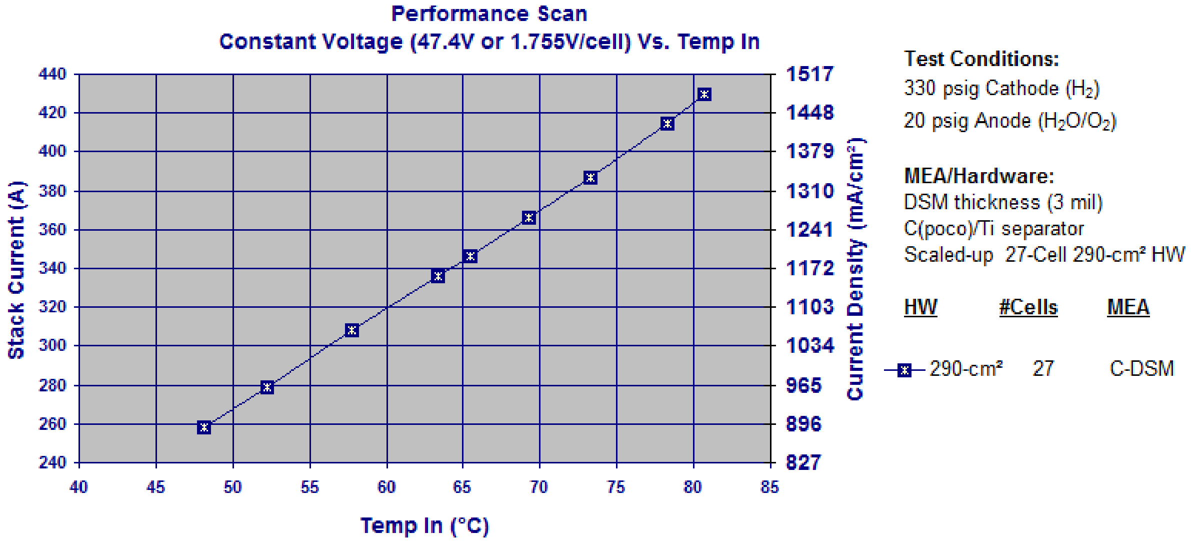


Figure 15. Constant Voltage Operation vs. Inlet Temperature

In conclusion, the performance of the scaled-up 27-cell electrolyzer stack, assembled with DSM-PFSA MEAs, exhibits high cell efficiency of 74%LHV (87.5% HHV) at current densities ≥1500 mA/cm², meeting DOE efficiency targets for stack performance. At the conclusion of this testing, the full scale 290 cm² 27-cell electrolyzer stack was shipped to Parker for installation into the electrolyzer system.

4.4 Electrolyzer System

To improve the system efficiency and reduce system cost, Giner teamed with Parker Hannifin (Parker). Parker is a manufacturer of commercial laboratory hydrogen generators and has significant experience in reducing the cost, while focusing on safety and reliability, of hydrogen systems. Parker worked with Giner to redesign the electrolyzer BOP to reduce component and fabrication cost and system power consumption, providing low-cost, commercial designs of components and control electronics. To demonstrate the BOP advances, Parker designed and fabricated an electrolyzer system for production of 0.5 kg/hr hydrogen. The system utilized the 290-cm^2 advanced electrolyzer stack developed during the program.

The system design went through a number of iterations and was subjected to a design review at the Parker facility with Giner personnel attending. Modifications that were identified during the design review were implemented and the system process and instrumentation diagram (P&ID) and process flow diagram (PFD) drafts completed. As part of the preliminary system design review, an extensive Safety Management Plan was drafted by Parker with the aid of an outside safety consultant; setting out the approach to planned safety management during the course of the system build, catering to both safety within the contracted program and for ensuring that any derived products will also be safe. Two safety workshops were held; first to identify hazards, accidents, and environmental impacts and the second being a consolidation workshop to identify those hazards and accidents which have a safety impact.

The electrolyzer system featured the 27-cell electrolyzer stack with an active area of 290 cm²/cell, producing hydrogen at pressures of 300-400 psig; a regenerative hydrogen dryer, maintaining hydrogen gas output at a dewpoint below -50°C; the integration, where feasible, of electrolyzer subsystems to minimize the number of BOP components, including a shared water loop between the stack feed and the deionized water cooling loops; and sensors for monitoring the product gases to prevent/detect formation of flammable/explosive mixtures. The power to the electrolyzer is supplied by a commercial DC power supply, converting AC grid power to the required DC stack voltage.

The electrolyzer system layout is shown in **Figure 16** (external layout) & **Figure 17** (internal layout). The layout is effectively broken into 3 zones, namely the oxygen (O_2) compartment, the hydrogen (H_2) compartment, and the electrical controller/power supply compartment. Compartments are isolated from each other. Ventilation fans are located in both the O_2 and H_2 compartments as shown in the 'top view'. The O_2 compartment contains the oxygen gas-phase separator, a circulating liquid pump, and the deionized (DI) water feed tank; the H_2 compartment, encloses the high and low pressure hydrogen gas-phase separators, heat exchanger, cooling fans, and various flow valves. The refrigeration unit, used to cool H_2 gas prior to entering the H_2-dryer, is located below the controller and adjacent the electronic power supply. The design incorporates the use of multiple panels that provide easy access during maintenance and/or repair.

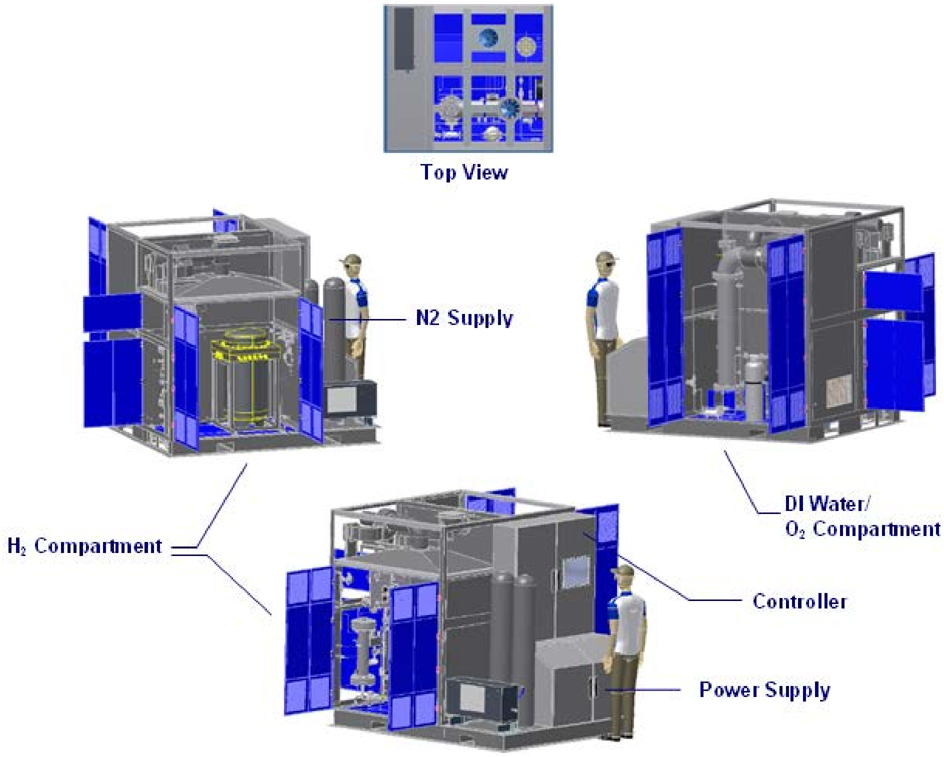


Figure 16. Electrolyzer System Layout

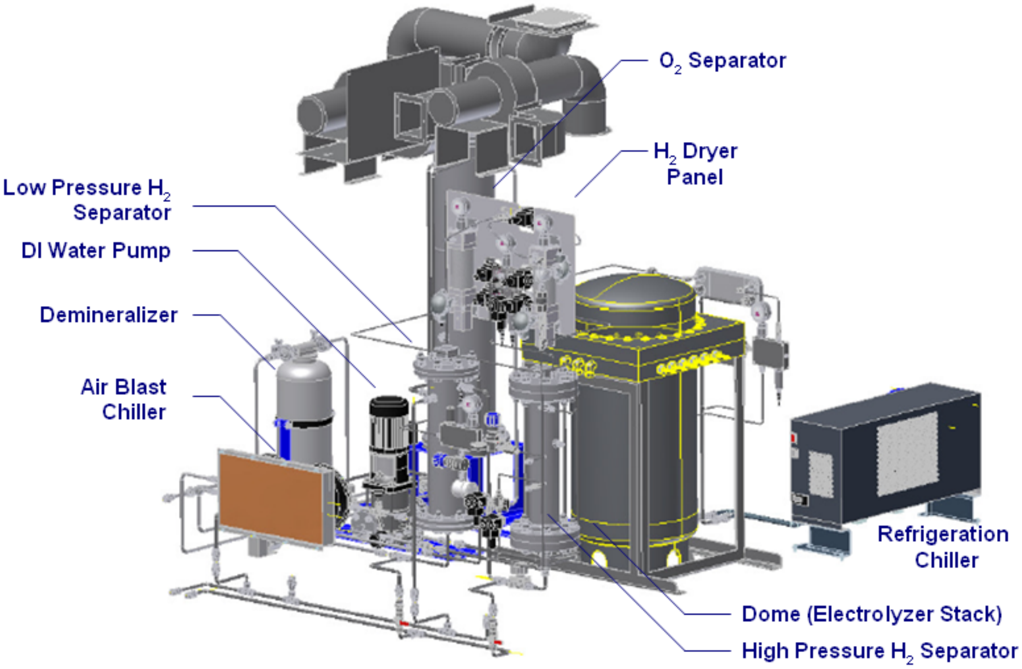
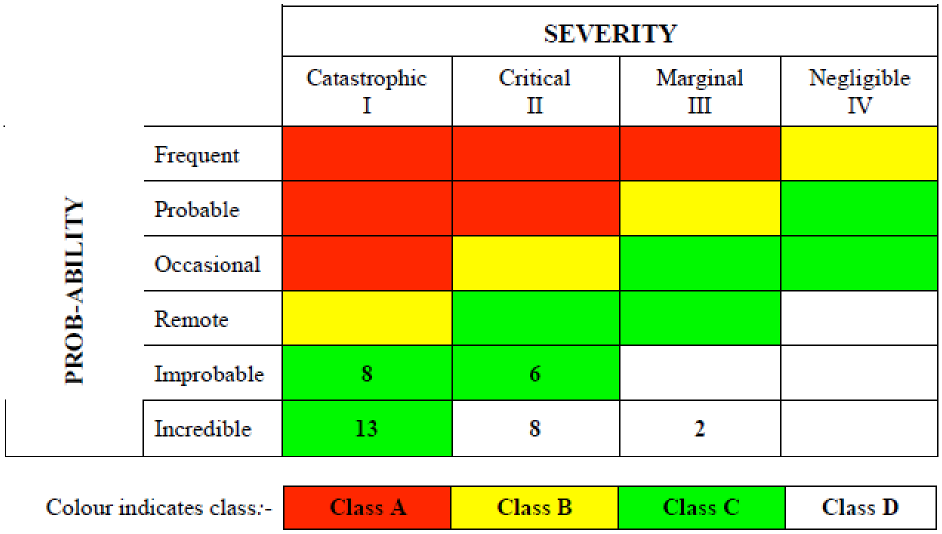


Figure 17. Internal Electrolyzer System Layout (walls removed)

During system operation, power and water are supplied to the electrolyzer stack. The stack operates at a differential pressure, i.e. hydrogen is generated at a pressure of 300-400 psig and oxygen near ambient pressure, reducing the safety requirements related to high-pressure oxygen production and storage. Water in the feed loop is circulated from the water-reservoir (which also functions as the oxygen-phase-separator) to the anode side of the electrolyzer stack and back to the water-reservoir via a circulating pump. This pump operates at low differential pressure, as it only needs to overcome the pressure drop in the feed loop. Oxygen generated on the anode side of the electrolyzer stack is separated from water in the oxygen-phase-separator, diluted with air, and then vented from the system. During electrolyzer operation water is also transferred from the anode side of the electrolyzer stack to the cathode side as a result of protonic drag through the membrane. The water that crosses over is collected in the high-pressure-hydrogen-phase-separator (HPHS) and returned to the electrolyzer feed loop after it has been degassed. Degassing is accomplished by transferring the protonic water to a low-pressure-hydrogen-phase-separator (LPHS) located in the hydrogen gas recirculation loop. Hydrogen from the HPHS is passed through the regenerative dryer prior to exiting the system where it can be stored in gas tanks for later use

A failure mode and effect analysis (FMEA) of the electrolyzer stack and system was jointly conducted by Giner and Parker. The severity of each FMEA node can be described by class. The highest severity cases are related to hydrogen ignition (Class A) due to plumbing leakages and stack failures. Another cause is by failure to detect hydrogen in an oxygen stream due to sensor failure. Also of concern are cases related to electrocution and electrical shorts (Class B). Less severe are Classes B and D that take into account sudden shutdown due to power failure, injuries due to water leakage, etc.… During the final safety review 546 possible scenarios were reviewed, and 489 control actions recognized and recorded within the hazard log. After the latest safety implementations, the remaining 37 scenarios were deemed improbable. The outcome of the FMEA analysis is summarized in **Table 3**, showing the cases in their probability/severity category. The electrolyzer system required detailed planning with respect to system layout and fabrication sequence. Several factors, including specific codes and standards that are pertinent to hydrogen electrolyzer systems were also considered during the system layout.

Table 3. FMEA Analysis



		SEVERITY			
		Catastrophic I	Critical II	Marginal III	Negligible IV
PROB-ABILITY	Frequent	🟥	🟥	🟥	🟨
	Probable	🟥	🟥	🟨	🟩
	Occasional	🟥	🟨	🟩	🟩
	Remote	🟨	🟩	🟩	
	Improbable	🟩 8	🟩 6		
	Incredible	🟩 13	8	2	

Colour indicates class:-	🟥 Class A	🟨 Class B	🟩 Class C	Class D

Number of Accidents by Probability/Severity Category, indicating Risk Class

The complete system build is shown in **Figure 18** and includes the following specifications:

- Dimensions:
    - 7.2′ H x 6.6′ L x 7.8′ W
        - 3 Compartments (H_2, O_2, and Power Supply/Controls)
        - System oversized to accommodate larger stacks
- Production Rate
    - 0.5 kg H_2/hr
    - 2.0 kg-H_2/hr (w/ larger Stack & Power Supply)
- Operating Pressure
    - H_2:300- 400 psig; O_2 atm
- Operating Temperature
    - 80°C
- Membrane
    - DSM-PFSA
- Stack Size
    - 290 cm^2/cell, 27 Cells
- Stack Current Density Operating Range
    - 1500-1900 mA/cm^2
- H_2 Dryer
    - Dual-column dryer to reduce maintenance and desiccant replacement

Figure 18. Electrolyzer Generator

4.4.1 Electrolyzer System Evaluation

The 0.5 kg-H_2/hr electrolyzer system was delivered and installed at NREL's National Wind Technology Center (NWTC) for validation. In addition to NREL's evaluation, multiple 100-hour trial runs were conducted on the electrolyzer system at the Parker facilities prior to delivery. An extensive operating and safety manual was also provided with the delivered unit. A safety checklist was completed by NREL, Parker, and Giner personnel prior to operation. The photographs in **Figure 19** and **Figure 20** illustrate the installation, operation, and testing of the electrolyzer unit at NREL. **Figure 21** illustrates the 100-hour test summary showing stack power, run time, and any major disturbances during operation and analysis period.

Figure 19. System Installation at NREL Facilities

Figure 20. Electrolyzer Stack (top), Oxygen Chamber (bottom left), and Hydrogen Dryer (bottom right)

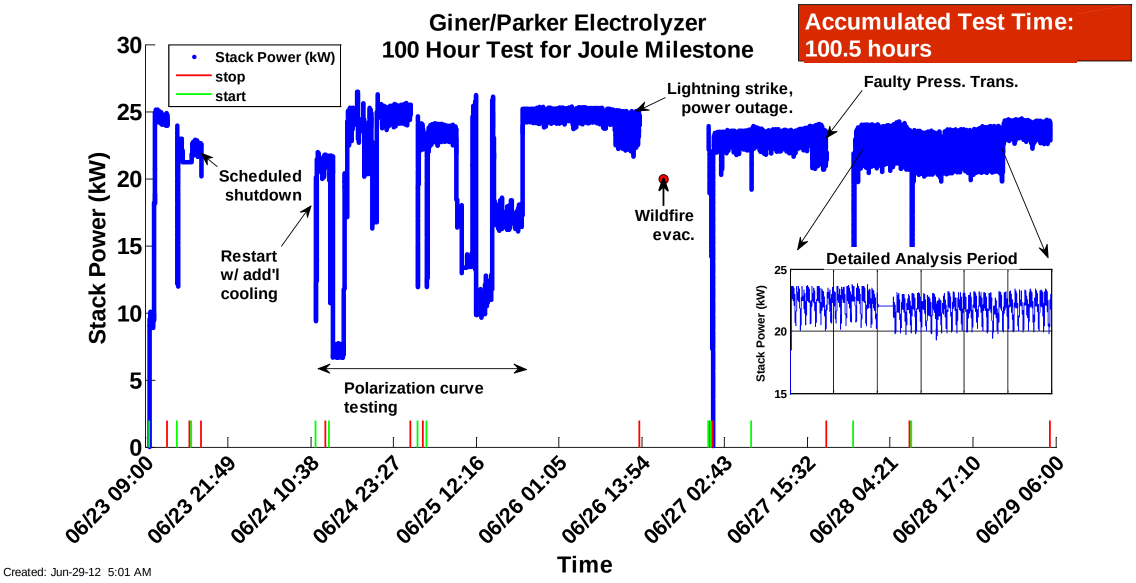


Figure 21. 100-Hour Summary Showing Electrolyzer Stack Power, Run Time, Major Disturbances and Detailed Analysis Period (Courtesy NREL)

At the nominal operating condition of 1500 mA/cm², 80°C, and 390 psig the efficiency of the 27-cell electrolyzer stack was measured at > 87% (HHV) by NREL, **Figure 22**. A polarization scan of the electrolyzer stack also indicates high cell voltage efficiencies in the current-density operating range of 250 to 1900 mA/cm². At a current density of 1,900 mA/cm², the stack efficiency was measured at >85% (HHV), and stack efficiencies > 90% (HHV) were measured at current densities below 1,000 mA/cm².

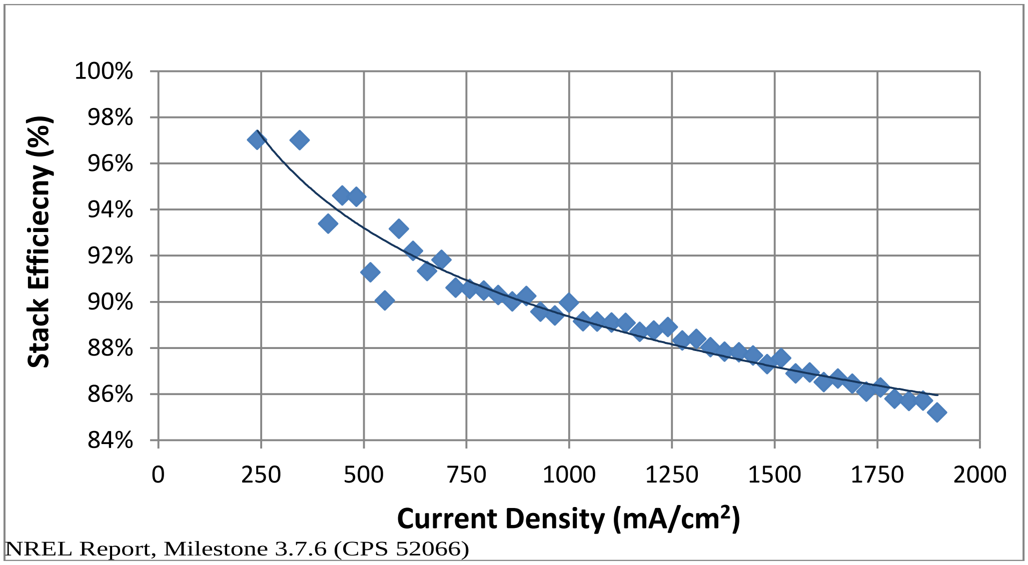


Figure 22. Stack Efficiency at Various Current Densities (NREL Report, Milestone 3.7.6)

The system and stack are designed to operate at 80°C. The energy or heat source required to maintain this operating temperature is supplied by the electrolyzer stack (heat generated as a resultant of stack inefficiency). At current densities below 1,000 mA/cm², the stack is very efficient (>90%HHV), and thus does not generate enough heat to maintain the 80°C operating temperature. Although not intended to operate below 1000 mA/cm², NREL was capable of measuring the stack efficiency of > 90% (HHV) below this current density. The stack efficiency at lower current density operation does not fit the trend exactly due to inadequate operation time at constant temperature (stack/system begins to cool).

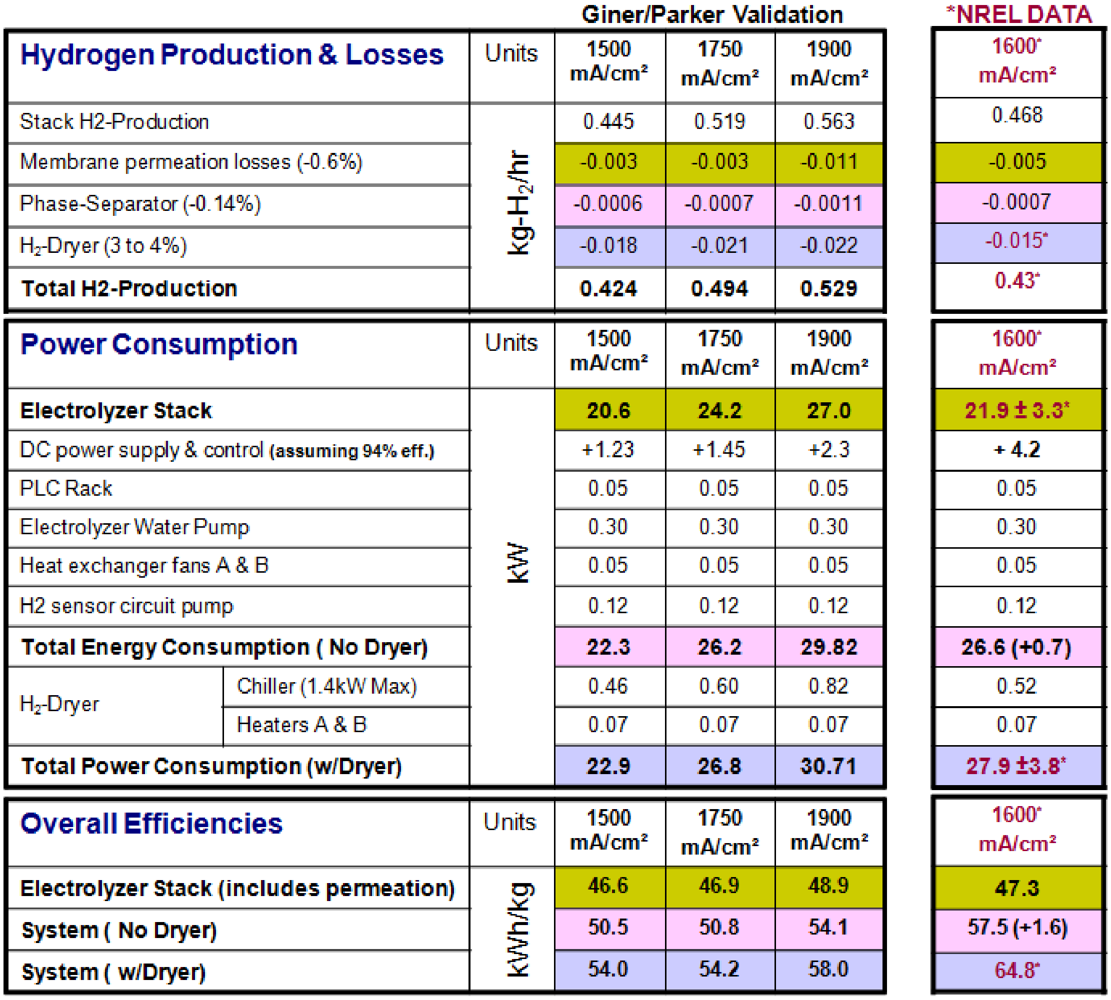
In summary, the 0.5 kg-H_2/hr electrolyzer system was successfully operated for 100 hours to complete a DOE Joule Milestone. NREL continued to evaluate the system and completed a 2nd DOE Milestone: "200 hours of testing and evaluation of the prototype electrolyzer system". During NREL's evaluation, electrolyzer stack efficiencies were measured at 85% (HHV) at a current density of 1900 mA/cm², >87% (HHV) at 1500 mA/cm², and > 90% (HHV) at current densities below 1000 mA/cm². The performance obtained by NREL confirms or exceeds the performance that was measured by Giner and Parker during initial stack evaluations.

4.4.2 Electrolyzer System Efficiency

An estimate of overall system efficiency was determined by analyzing the power consumption of the various system components and the hydrogen-generation rate (and losses) throughout the electrolyzer system, **Table 4**. Hydrogen losses occur in three separate areas of the system. This includes hydrogen losses due to gas permeation through the membrane, degassing from the phase-separator, and during the hydrogen drying phase. The power-consumption values shown in Table 4 are based on component ratings and intermittent operation of the chiller, heat-exchanger fans, and desiccant heaters. The power supply efficiency rating of 94% was used and is based on actual manufacturer's rating. Although the system utilizes oversized components to accommodate the use of larger stacks (up to 2 kg H_2/hr), system efficiency was not impacted.

As measured by NREL, the overall power consumption of the electrolyzer System was 65 kWh_e/kg-H_2. Although the overall power consumption is higher than initial targets, this was not unexpected. The overall system efficiency includes loses related to the main power supply. As measured by NREL, the efficiency of the 'off-the-shelf' power supply was measured at 78%. This efficiency was much lower than that specified by the manufacturer of 94%. The lower power supply efficiency, and the use of safety ventilation fans, introduces an additional 5.85 kWe power requirement (or an additional efficiency loss of 11.7% (HHV)). With an appropriate power supply that operates in the suggested efficiency range of 94%; the overall system power consumption is estimated at 54.0 kWh/kg-H_2 at an operating current density of 1500 mA/cm², 54.2 kWh/kg-H_2 at 1750 mA/cm², and 58.0 at 1,900 mA/cm². In addition, the efficiency of the hydrogen dryer measured by NREL was 96.6% (3.4% loss of the total hydrogen generated). As a comparison, the industrial standard for hydrogen dryers is 85-90% (10-15% loss).

Table 4. Electrolyzer Efficiency



		Giner/Parker Validation			*NREL DATA
Hydrogen Production & Losses	Units	1500 mA/cm²	1750 mA/cm²	1900 mA/cm²	1600* mA/cm²
Stack H2-Production	kg-H_2/hr	0.445	0.519	0.563	0.468
Membrane permeation losses (-0.6%)		-0.003	-0.003	-0.011	-0.005
Phase-Separator (-0.14%)		-0.0006	-0.0007	-0.0011	-0.0007
H_2-Dryer (3 to 4%)		-0.018	-0.021	-0.022	-0.015*
Total H2-Production		**0.424**	**0.494**	**0.529**	**0.43***

Power Consumption	Units	1500 mA/cm²	1750 mA/cm²	1900 mA/cm²	1600* mA/cm²
Electrolyzer Stack	kW	**20.6**	**24.2**	**27.0**	**21.9 ± 3.3***
DC power supply & control **(assuming 94% eff.)**		+1.23	+1.45	+2.3	**+ 4.2**
PLC Rack		0.05	0.05	0.05	0.05
Electrolyzer Water Pump		0.30	0.30	0.30	0.30
Heat exchanger fans A & B		0.05	0.05	0.05	0.05
H2 sensor circuit pump		0.12	0.12	0.12	0.12
Total Energy Consumption (No Dryer)		**22.3**	**26.2**	**29.82**	**26.6 (+0.7)**
H_2-Dryer: Chiller (1.4kW Max)		0.46	0.60	0.82	0.52
H_2-Dryer: Heaters A & B		0.07	0.07	0.07	0.07
Total Power Consumption (w/Dryer)		**22.9**	**26.8**	**30.71**	**27.9 ±3.8***

Overall Efficiencies	Units	1500 mA/cm²	1750 mA/cm²	1900 mA/cm²	1600* mA/cm²
Electrolyzer Stack (includes permeation)	kWh/kg	**46.6**	**46.9**	**48.9**	**47.3**
System (No Dryer)		**50.5**	**50.8**	**54.1**	**57.5 (+1.6)**
System (w/Dryer)		**54.0**	**54.2**	**58.0**	**64.8***

4.5 Economic Analysis

At the program completion and with the electrolyzer system finalized, cost structures can be modeled with a higher degree of accuracy. In 2011, Giner conducted a cost analysis of its hydrogen generating PEM-based electrolyzer technology using the DOE H2A model version 2.1.1 for distributed production. Utilizing the same cost structures from 2011, the hydrogen cost analysis was repeated using the latest H2A model: *02D H2A Distributed Hydrogen Production Model version 3.0*. The difference in the models relates to the reference year that determines the base-year dollars used, i.e. the nominal-year currency in which hydrogen costs are reported. In version 2, the reported hydrogen costs are in 2005 dollars, version 3; 2007 dollars. Additionally, version 3 reflects increases in the cost of industrial electricity ($0.039/kW to $0.057/kW), installation factor (1.10 to 1.17), project contingency (10% to 15%), labor costs ($15 to $50), cost of demineralized water ($0.000079/gal to 0.0054/gal), and hydrogen compression (6250 psia to 12,688 psia)[7].

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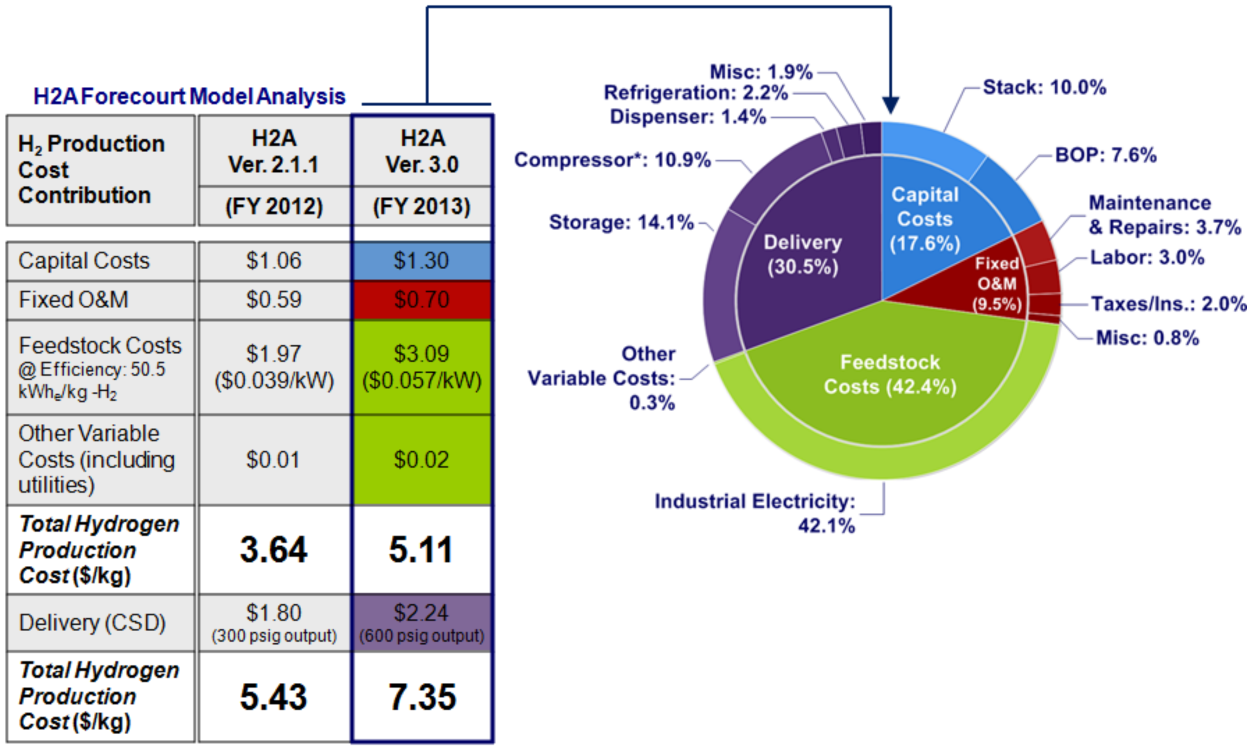
[7] NREL, H2A Central Hydrogen Production Model, Version 3 User Guide (DRAFT),D. Steward, T. Ramsden, J. Zuboy

Hydrogen production costs are based on the evaluation of the 27-cell, scaled-up electrolyzer stack utilizing dimensionally stable membranes and the power consumption of BOP components utilized in the system. The cost estimate also assumes that the system is operating with a source of compressed inert gas, thus eliminating the hydrogen-dryer losses of 3-4% and related power consumption of the chiller (in smaller systems).The results indicate that the largest cost component of the production cost is the feedstock followed by compression, storage, and dispensing (CSD). Significant reductions in electrolyzer system feedstock costs are made with the higher-efficiency membranes fabricated in this program. The feedstock cost of an electrolyzer system operating with a 3 mil DSM-PFSA membrane, efficiency of 87% HHV, is $1.97; for comparison the feedstock cost of an electrolyzer system operating with Nafion 117 (cell efficiency of 78%-HHV @ 80°C), is calculated to be $2.25.

The preliminary cost structures that have been used are associated with hydrogen produced at the level required for a forecourt station. The estimated costs of hydrogen ($/kg-$H_2$) using the H2A Model (ver. 2.1.1 & 3.0) are shown in **Table 5.** A breakdown of the H_2 costs utilizing H2A ver. 3.0 is also provided. The results are based on the following assumptions:

- Design capacity: 1500 kg H_2/day
- Large-scale production- costs for 500th unit
- PEM-based electrolyzer technology for hydrogen generation
- Industrial electricity at $0.039/kWh (ver. 2.1.1) and $0.057/kWh (ver. 3.0)

Table 5. H2 Cost Analysis



H2A Forecourt Model Analysis

H_2 Production Cost Contribution	H2A Ver. 2.1.1 (FY 2012)	H2A Ver. 3.0 (FY 2013)
Capital Costs	$1.06	$1.30
Fixed O&M	$0.59	$0.70
Feedstock Costs @ Efficiency: 50.5 kWh$_e$/kg -H_2	$1.97 ($0.039/kW)	$3.09 ($0.057/kW)
Other Variable Costs (including utilities)	$0.01	$0.02
Total Hydrogen Production Cost ($/kg)	**3.64**	**5.11**
Delivery (CSD)	$1.80 (300 psig output)	$2.24 (600 psig output)
Total Hydrogen Production Cost ($/kg)	**5.43**	**7.35**

At present the total cost of producing hydrogen (CSD not included) ranges from $3.64-5.11/kg-$H_2$ depending on which of the H2A models is used. The progress made here is in line with achieving the new 2015 DOE target of $3.90/kg-H2 (CSD not included). To meet the 2020 DOE target of <\$3.00/ kg-H_2, the study indicates the need to further enhance system efficiencies, but also significantly reduce capital costs associated with CSD. Although feedstock is the largest fraction in the cost of producing hydrogen, CSD will require the largest reduction in cost to achieve future DOE targets.

5.0 CHANGES IN APPROACH OR AIMS

None.

6.0 PROBLEMS

The electrolyzer stack initially utilized a safety-dome enclosure (**Figure 23**). During pressure testing, gas leakage was detected at the electrical cable enter points located on the top dome plate. In order to avoid repair delays, the stack was removed from the dome and shipped to Parker for insertion into the system. In order to maintain the safety aspect that the dome provided, the system was modified with lockouts that disconnect electric to stack when the compartment doors are opened during operation. In addition, a ventilation blower in the system's chamber that encloses the electrolyzer stack was added to dilute accumulation of hydrogen in the case of leakage. Giner also verified the stack to twice the operating pressure. Via the system modifications and pressure testing, the safety codes and standards for hydrogen generators were satisfied and Parker commenced with system assembly and evaluation.

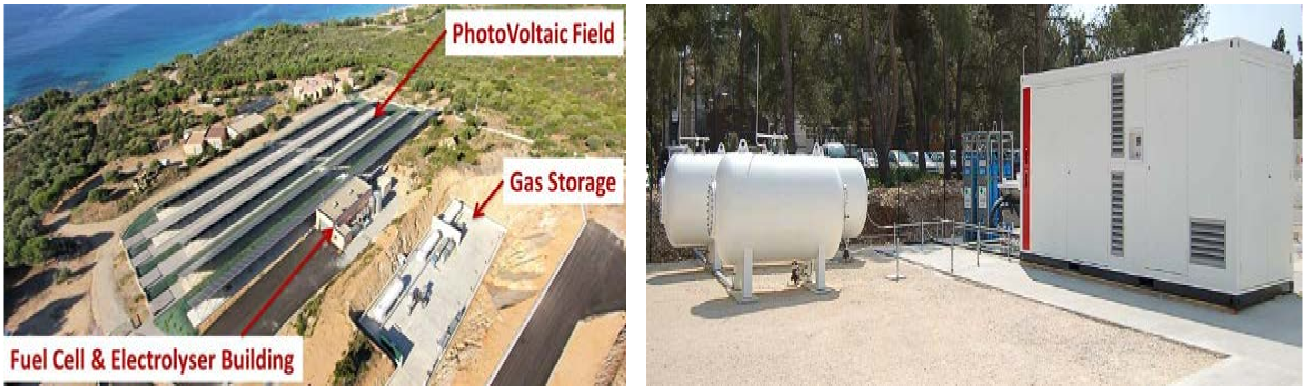
Figure 23. Assembled Stack & Dome

7.0 ABSENCE OR CHANGES IN KEY PERSONNEL

At the start of the program, the principle investigator was changed from Cecelia Cropley, Project Director, to Monjid Hamdan, Director of Engineering. Mr. Hamdan's expertise is in the design and development of electrochemical systems that include PEM-based electrolyzers and fuel cells. He has more than 20 years of experience in the field of PEM fuel cells & electrolyzers and holds several US patents in the related field.

8.0 PRODUCTS PRODUCED OR TECHNOLOGY TRANSFER ACTIVITIES

Giner Inc., a world-leader in proton-exchange-membrane (PEM)-based water electrolysis technology, has been developing and demonstrating cost-effective renewable energy-based PEM electrolyzers for electrolytic generation of hydrogen for both military and commercial applications. Under this recent DOE program (*DE-FG36*-08GO18065), Giner has developed a novel, highly efficient, low-cost, PEM-based Electrolyzer Stack for hydrogen production. The electrolyzer stack developed during this program was commercialized and is in production in cell configurations of 30-, 60-, and 100-cells. The product range will be broadened in the near-term future to include multi-cell stacks in the range of 200+ cells/stack. The stack technology has been demonstrated in laboratory-scale testing at Giner, and via commercial customer validation assessments. An example of the use of the low-cost Giner stack developed during this program for the integration of renewable energy sources is shown in **Figure 24**.



Giner, Inc.
Low-Cost
Electrolyzer Stack

Figure 24. AREVA's energy storage platform 'GREENERGY BOX' in Corsica, France Utilizing Giner, Inc. Electrolyzer Stack

9.0 LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

BOP	balance of plant
BPSH	biphenyl sulfone
C-DSM™	dimensionally stable membrane fabricated with a chemically etched support
CSD	compression, storage, and dispensing
DSM™	dimensionally stable membrane
EW	equivalent weight
FMEA	failure mode effect analysis
FRR	fluoride release rate
Giner	Giner, Inc.
HHV	higher heating value
HPHS	high-pressure hydrogen-phase-separator
LHV	lower heating value
LPHS	low-pressure hydrogen-phase-separator
NREL	National Renewable Energy Laboratory
NWTC	National Wind Technology Center
P&ID	process and instrumentation diagram
Parker	Parker Hannifin Corporation
PEM	proton-exchange membrane
PFD	process flow diagram
PFSA	perfluorosulfonic acid ionomer
ppb	parts per billion
psid	differential pressure (lb/in^2)
RH	relative humidity
VT	Virginia Polytechnic Institute and University
μ	micron