

II.D.1 PEM Electrolyzer Incorporating an Advanced Low-Cost Membrane

Monjid Hamdan (Primary Contact), Tim Norman
Giner, Inc. (Formerly Giner Electrochemical Systems, LLC.)
89 Rumford Ave.
Newton, MA 02466
Phone: (781) 529-0526
Email: mhamdan@ginerinc.com

DOE Managers

HQ: Erika Sutherland
Phone: (202) 586-3152
Email: Erika.Sutherland@ee.doe.gov
GO: David Peterson
Phone: (720) 356-1747
Email: David.Peterson@go.doe.gov

Contract Number: DE-FG36-08GO18065

Subcontractors:

- Virginia Polytechnic Institute and University, Blacksburg, VA
- Parker Hannifin Ltd donnick hunter Division, Hemel Hempstead, United Kingdom

Project Start Date: May 1, 2008
Project End Date: January 31, 2013

Fiscal Year (FY) 2012 Objectives

Develop and demonstrate advanced low-cost, moderate-pressure polymer electrolyte membrane (PEM)-based water electrolyzer system to meet DOE targets for distributed electrolysis:

- Develop high-efficiency, low-cost membrane
- Develop long-life cell-separator
- Develop lower-cost prototype electrolyzer stack and system
- Demonstrate prototype at the National Renewable Energy Laboratory (NREL)

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (G) Cost - Capital Cost
- (H) System Efficiency

Technical Targets

Giner Progress toward Meeting DOE Targets for Distributed Electrolysis Hydrogen Production¹

Characteristics	Units	2015/2017 Target	2012 Giner Status
Hydrogen Production Cost ²	\$/kg H ₂	3.30/<2.70	3.64
Electrolyzer Capital Cost	\$/kg H ₂	0.70/0.30	0.60 ³ (1.06) ⁴
Electrolyzer Energy Efficiency	% (LHV ⁵)	69/74	66 ⁶

¹ Using H2A model rev 2.1.1. Based on electricity cost of \$0.04/kWh.

² Production only (H₂ compression, storage, and delivery expected to add \$2.00/kg).

³ Electrolyzer stack

⁴ Electrolyzer system (stack & BOP)

⁵ Lower heating value

⁶ Does not include H₂-dryer. Stack efficiency measured at 74% LHV.

FY 2012 Accomplishments

Membrane:

- Demonstrated enhanced dimensionally stable membrane (DSM™) performance.
- Completed 5,000-hour life-test with DSM™ (@80°C, 300 psid).
- DSM™ operating lifetime estimated at 55,000 hours.
- Reduced membrane support cost by one order of magnitude.

Cell-Separator:

- Demonstrated reduced hydrogen embrittlement in titanium/carbon cell-separator.
- Projected longevity of the carbon/titanium cell-separators (>60,000 hours).

Electrolyzer Stack and System Design:

- Completed fabrication of full-scale electrolyzer stack utilizing low-cost components.
- Reduced electrolyzer stack costs by 60%.
- Commercialized electrolyzer stack in 2011. Electrolyzer stacks field tested at customer locations (>1,000 hours).
- Completed fabrication of electrolyzer system incorporating a high-efficiency H₂-dryer.
- Extensive safety review of electrolyzer system completed.

- Completed modeling of electrolyzer capital and operating costs; performed economic analysis using the DOE H2A model illustrating cost-reductions.
- Delivered and demonstrated prototype electrolyzer system at NREL.



Introduction

The 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, state-of-the-art electrolyzers are not economically competitive for forecourt hydrogen production due to their high capital and operating costs. The cost of hydrogen produced by present commercially available electrolysis systems is estimated to be \$4.80/kg-H₂, considerably higher than the DOE target of <\$3.00/kg-H₂ by 2017 [1]. Analysis of electrolyzer systems performed by Giner and others using DOE's H2A model indicate that the major cost elements are the cost of electricity, the capital costs of electrolyzer stacks and systems, and the high cost of hydrogen compression, storage, and delivery.

Giner, Inc. (Giner) has developed proton exchange membrane (PEM)-based electrolyzer technology that operates at differential pressure for producing hydrogen at moderate to high pressure directly in the electrolyzer stack, while oxygen is evolved at near-atmospheric pressure. The goals of the project are to reduce the cost of the stack and system, improve electrolyzer efficiency, and to demonstrate electrolyzer operation at moderate pressure.

Approach

To reduce the cost of producing hydrogen, Giner is improving electrolyzer stack efficiency and reducing stack cost through development of an advanced low-cost, high-strength, membrane that utilizes a perforated polyimide support imbibed with perfluorosulfonic acid (PFSA) ionomer. Giner is also reducing stack capital cost and increasing stack life through development of a long-life bipolar stack cell-separator, decreasing stack costs by initiating scale-up to a larger active area, and reducing the system capital cost by applying commercial production methods to PEM-based electrolyzer systems. In each of the key development areas, Giner and its team members are conducting focused development of advanced components in laboratory-scale hardware, followed by life-testing of the most promising candidate materials.

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 the hydrogen economy.

Results

DSM™ Membrane Performance

To improve electrolyzer efficiency, Giner has developed an advanced supported membrane having an ionic resistance comparable to that of a 0.0020 to 0.0035 inch-thick Nafion® [2] membrane, but having significantly improved mechanical properties. This advanced membrane is referred to as a DSM™ 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 (Kapton®) base film with a definable open pattern. The support structure is then imbibed with 1100-equivalent-weight PFSA ionomer to a thickness of 3 mil (0.003"). Initially, Giner fabricated the membrane support structures using a laser-drilling procedure. In 2011, a more cost-effective technique of fabricating the support structures via chemical-etching was implemented by Giner, reducing the cost of the membrane by one order of magnitude.

Polarization scans of the DSM™ were conducted in scaled-up, 27-cell electrolyzer stack hardware, through a current density range of 0-1,750 mA/cm², a differential pressure of 300 psid, and a temperature of 80°C. The average cell voltage was measured at 1.757 V/cell corresponding to a voltage efficiency of 74% LHV (87% higher heating value) at a current density of 1,500 mA/cm², Figure 1. During testing, the DSM™ exceeded the criterion for performance:

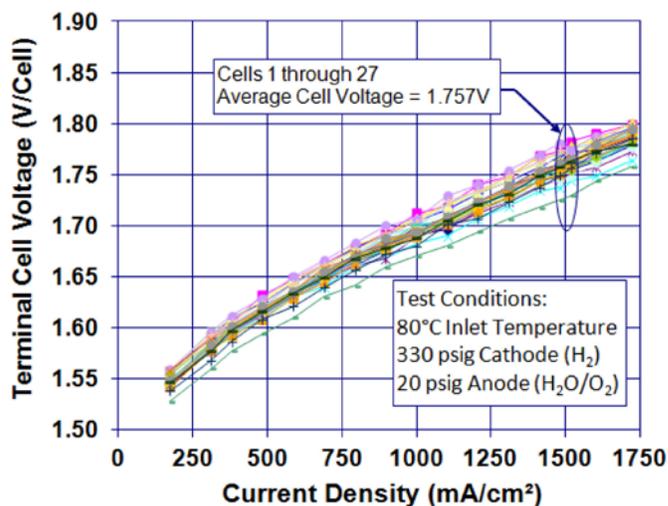


FIGURE 1. Membrane Performance in Full-Scale Electrolyzer Stack Hardware

exhibiting lower cell voltages and thus higher cell efficiencies than that of a Nafion® 1135 membrane.

Durability of the DSM™ was also demonstrated in the scaled-up, hardware via fluoride release rate (FRR) measurements at constant-current operation. Since PFSA ionomer is used as the membrane material and in the binder for the catalyst layer, the loss of fluoride is used as a measurement of membrane degradation. An FRR rate of $3.7 \mu\text{g F}^- \text{ ion/hr}$ or less than $10 \text{ micrograms F}^- \text{ ion/L}$ (<10 ppb) was present in the cathode effluent (electro-osmotically transported water) at the end of 1,000 and 5,000-hour life tests. Based on electrolysis FRR results, the lifetime of the DSM™ is projected to be between 45,000 and 55,000 hours.

Cell-Separator Development

The cell separator is a gas-impermeable conductive sheet that separates the hydrogen and oxygen compartments in the bipolar stack. The separator must be highly conductive, as well as resistant to hydrogen embrittlement and to corrosion in an oxidizing environment. Giner's legacy high-pressure naval electrolyzers use a complex multi-layer cell-separator incorporating a conductive compliant member and sheets of niobium and zirconium metal. Zirconium is used due to its high resistance to hydrogen embrittlement. Giner has previously evaluated a low-cost, dual-layer titanium cell-separator. Although performance was comparable to that of niobium/zirconium cell-separators, lifetimes were limited to 5,000 hours due to hydrogen embrittlement.

The most promising approach for long-term implementation has been achieved 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/titanium cell

separator in scaled-up 290-cm² electrolyzer stack hardware. Performance is comparable to that of the niobium-zirconium separator. In addition, life expectancy of the carbon/titanium separator, determined via hydrogen-uptake analysis over a 5,000-hour period, indicates lifetimes exceeding the 50,000-hour system requirement.

Electrolyzer Stack and System Fabrication

In addition to the use of chemically etched DSM™ and carbon/titanium cell-separators, the electrolyzer stack includes several modifications to Giner's legacy hardware; (1) an increase in cell active area from 160 to 290 cm², effectively reducing the number of cells required to produce a given amount of hydrogen, thus reducing the stack manufacturing labor, (2) an overall decrease in the parts count per cell (from 41 to 10), (3) a 75% reduction in anode and cathode catalyst loadings, (4) molded thermoplastic cell frames, resulting in a cost reduction of 95% as compared to machining this component, (5) a 33% reduction in cell frame thickness, thus reducing the anode and cathode support materials and costs by 33%, and (6) a low-cost carbon-steel end plate. As a result of the component and membrane development during this program, the overall projected capital cost of the electrolyzer stack alone has decreased from greater than \$1,000/kW in 2007 to <\$350/kW in 2011 (Figure 2).

The electrolyzer system, shown in Figure 3, 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 considered during the system

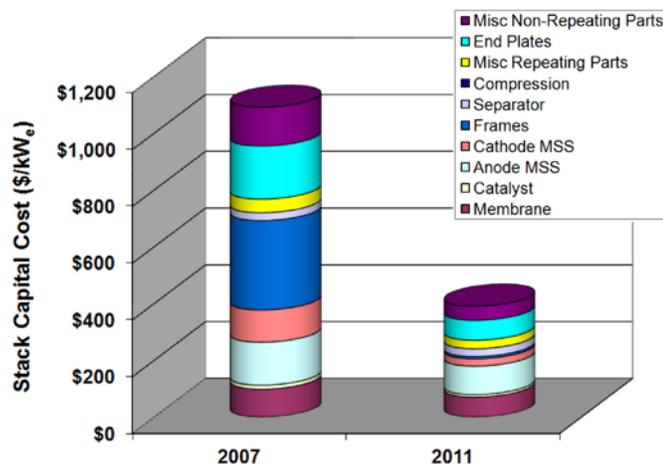


FIGURE 2. Electrolyzer Stack Capital Costs



FIGURE 3. Electrolyzer System

layout. To meet these requirements, the system was designed with three separate compartments; the oxygen (O₂), the hydrogen (H₂), and the electrical (controller and power supply) compartments. The O₂ compartment contains the oxygen gas-phase separator, a circulating liquid pump, and the deionized water feed tank. The H₂ compartment encloses a novel high-efficiency (97%) hydrogen dryer assembly, high- and low-pressure hydrogen gas-phase separators, a heat exchanger, cooling fans, and various flow valves. The electrolyzer stack is powered via a high-efficiency power supply rated at 94% located in the electrical compartment.

The system build, undertaken at the Parker facility, was delivered and tested at NREL's National Wind Technology Center in 2012. A breakdown of the system performance and efficiencies during the initial evaluation period is shown in Table 1. At an operating current density of 1,500 mA/cm², the electrolyzer stack exhibits an energy efficiency of 46.6 kWh/kg, the overall system (not including the H₂-dryer); 50.5 kWh/kg, and with the H₂-dryer; 54.0 kWh/kg. The H₂-dryer utilizes dry hydrogen as a carrier gas. Although the H₂-dryer operates at a high efficiency as compared to the industrial

standard (~10% loss), this is not indicative of a forecourt station where nitrogen is typically used as a carrier gas. It is thus feasible to operate scaled-up systems of this type in the range of 50.5 kWh/kg. During testing at NREL, the voltage performance of the electrolyzer stack was verified, in addition to H₂-dryer losses of less than 3%.

Conclusions and Future Directions

Significant progress has been made in DSM™ membrane development. Giner has demonstrated membrane reproducibility and durability as well as a significant improvement in electrolyzer cell efficiency. The progress made during this program is in line with achieving DOE's 2017 efficiency targets. In addition, development efforts conducted under this project have resulted in significant cost reductions of PEM-based electrolyzer stacks and systems, an increase in the life of the low-cost cell-separators, and improved BOP components efficiency. The future objectives are to:

- Complete evaluation of prototype electrolyzer system at NREL.
- Continue investigation of low-cost stack and system components.
- Conduct optimization studies for stack and system, including the H₂-dryer.
- Develop a high-pressure (>5,000 psi) electrolyzer stack design utilizing low-cost components developed during this project

TABLE 1. Electrolyzer System Performance

Hydrogen Production & Losses	Units	1,500 mA/cm ²	1,750 mA/cm ²
Stack H ₂ -Production	kg-H ₂ /kg	0.445	0.519
Membrane permeation losses (-0.6%)		-0.003	-0.003
Phase-Separator (-0.14%)		-0.0006	-0.0007
H ₂ -Dryer (- 3 to 4%)		-0.018	-0.021
Total H₂-Production (@STP)		0.424	0.494

Power Consumption	Units	1,500 mA/cm ²	1,750 mA/cm ²
Electrolyzer Stack	kW	20.6	24.2
Direct current power supply & control (assuming 94% eff.)		+1.23	+1.45
PLC Rack		0.05	0.05
Electrolyzer water pump		0.30	0.30
Heat exchanger fans A & B		0.05	0.05
H ₂ sensor circuit pump		0.12	0.12
Total Energy Consumption (No Dryer)		22.3	26.2
H ₂ -Dryer		0.53	0.67
Total Energy Consumption (w/Dryer)		22.9	26.8

Overall Efficiencies	Units	11,500 mA/cm ²	1,750 mA/cm ²
Electrolyzer Stack (includes permeation)	kWh/kg	46.6	46.9
System (No Dryer)		50.5	50.8
System (w/Dryer)		54.0	54.2

Special Recognitions

1. 2012 DOE Hydrogen and Fuel Cells Program R&D Award

FY 2012 Publications/Presentations

1. M. Hamdan, *PEM Electrolyzer Incorporating an Advanced Low-Cost Membrane*. 2012 Hydrogen Annual Program Merit Review Meeting. Presentation #pd_030_hamdan, May 16, 2012.
2. M. Hamdan, *Unitized Design for Home Refueling Appliance for Hydrogen Generation to 5,000 psi*. 2012 Hydrogen Annual Program Merit Review Meeting. Presentation #pd_065_norman, May 15, 2012.

References

1. Multi-Year Research, Development and Demonstration Plan. Hydrogen Production. DOE, Pg 3.1-14 (2011 Interim Update) <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf>
2. Nafion® and Kapton® are registered trademarks of E.I. du Pont de Nemours and Company