

II.E.2 PEM Electrolyzer Incorporating an Advanced Low-Cost Membrane

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Subcontractors:

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

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 Project End Date: April 30, 2012

Objectives

- Develop and demonstrate advanced low-cost, moderate-pressure proton exchange 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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

GES Progress toward Meeting DOE Targets for Distributed Electrolysis Hydrogen Production

Characteristics	Units	2012/2017 Targets	GES Status
Hydrogen Cost	\$/kg H ₂	3.70/<3.00	4.95*
Electrolyzer Capital Cost	\$/kg H ₂	0.70/0.30	1.29
	\$/kW _e	400/125	463
Electrolyzer Energy Efficiency	% (LHV)	69/74	75

*Using H2A model rev 2.1.1. A cost of \$1.80 is included for H₂ compression, storage, and delivery
 LHV - lower heating value

Accomplishments

- Membrane
 - Demonstrated enhanced dimensionally stable membrane (DSM™) performance (>Nafion® [1] 1135 membrane)
 - Completed 1,000-hour life-test with DSM™ (@ 80°C)
 - 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)
- Preliminary Electrolyzer Stack and System Design
 - Completed electrolyzer stack and system design utilizing low-cost components
 - Completed process and instrumentation diagram, process flow diagram (PFD), system control diagrams and layout drawings
 - Completed extensive safety review of electrolyzer system
 - Completed modeling of electrolyzer capital and operating costs; performed economic analysis using the DOE H2A model illustrating cost-reductions.



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, 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 \$3.70/kg-H₂ by 2012 [2]. Analysis of electrolyzer systems performed by GES and others using the DOE 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.

GES has developed 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. In this system, liquid water, which is a reactant as well as coolant, is introduced into the oxygen side 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 PEM-based electrolyzers, GES is improving electrolyzer stack efficiency and reducing stack cost through development of an advanced low-cost, high strength, membrane using a perforated polyimide support imbibed with perfluorosulfonic acid (PFSA) ionomer. GES 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, GES 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. The project will culminate in fabrication and testing of an electrolyzer system for production of 0.5 kg-H₂/hr and validation of the electrolyzer stack and system in testing at NREL.

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, GES has developed an advanced supported membrane having an ionic resistance comparable to that of a 0.0020- to 0.0035-inch-thick Nafion® membrane, but having significantly improved mechanical properties. This advanced membrane is referred to as a dimensionally stable membrane (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® [1]) base film with a definable open pattern. Two separate techniques were employed in the fabrication of the DSM™ support. This includes membranes fabricated with a laser-drilled support (L-DSM™) and those with a recently developed low-cost chemically etched support (C-DSM™), Figure 1. The support structures are then imbibed with 850 and 1100 equivalent weight (EW) PFSA ionomer to a thickness of 3 mil (0.003”).

Polarization scans of the DSM™ were conducted through a current density range of up to 3000 mA/cm², a differential pressure of 300 psid, a temperature of 80°C, and with similar cathode and anode electrode structures. Results were compared to Nafion® 1135, Figure 2. During testing, both L-DSM™ and C-DSM™ exceeded the criterion for performance: each membrane exhibited lower cell voltages and thus higher cell efficiencies than that of a Nafion® 1135 membrane. In a direct comparison of DSM™ support structures imbibed with 1100 EW PFSA ionomer, L-DSM™ slightly outperforms C-DSM™. At an operating current density of 1,500 mA/cm², the performance of the L-DSM™ is 1.72 V, C-DSM™, 1.75 V. The slight loss in performance

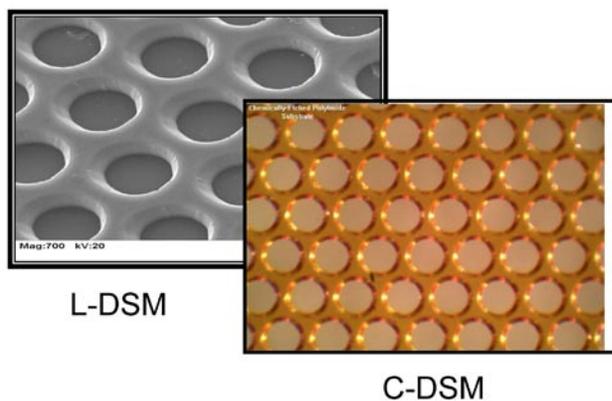


FIGURE 1. Micrograph of DSM Support Structures

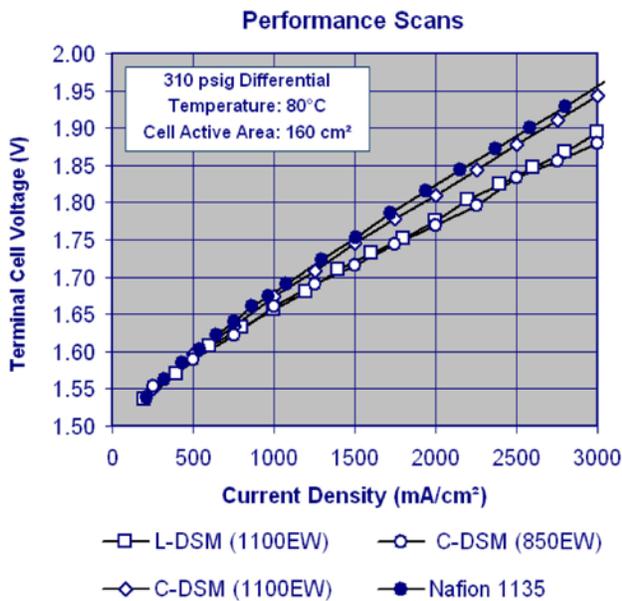


FIGURE 2. Performance Scans: L-DSM vs. C-DSM

of the C-DSM™ is attributed to the larger landing width within the chemically etched support structure resulting in an increase of the proton-transport path and thus restricting the proton-transport kinetics. The loss in performance of the C-DSM™ is overcome using a lower EW PFSA ionomer, namely 850 EW. It has been shown that the performance of the “low-cost” C-DSM™ (850 EW) is equivalent to that of the L-DSM™ (1100 EW) as noted;

$$\text{L-DSM (1100 EW)} = \text{C-DSM (850 EW)} > \text{C-DSM (1100 EW)}$$

Durability of the DSM™ was also demonstrated in full-size 160-cm² active area 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 μg F⁻ ion/hr or less than 10 micrograms F⁻ ion/L (<10 ppb) was present in the cathode effluent (electro-osmotically transported water) at the end of the 1,000-hour life test. Based on electrolysis FRR results, the lifetime of the DSM™ is projected to be between 45,000 and 55,000 hours, which exceed the durability requirements of the electrolyzer system. In addition to its durability, the DSM™ exhibits high cell efficiencies in the range of 75% LHV (88.8% higher heating value) at an operating current density of 1,500 mA/cm².

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. The proven GES high-pressure naval electrolyzer uses a complex multi-layer separator incorporating a conductive compliant member and sheets of niobium and zirconium metal. Zirconium is used due to its high resistance to hydrogen embrittlement. GES 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, GES demonstrated performance of a low-cost carbon/titanium separator in 160-cm² hardware comparable in performance to a dual-layer titanium separator at 1/40th the cost of niobium-zirconium cell-separators. In addition, life expectancy of the carbon/titanium separator, determined via hydrogen-uptake analysis over a 500-hour period, indicates lifetimes exceeding the 50,000-hour system requirement.

Preliminary Electrolyzer Stack and System

Design: As a result of the component and membrane development conducted in this project, the overall projected capital cost of the electrolyzer stack has decreased from greater than \$2,500/kW in 2001 to \$463/kW in 2010, with a further projected decrease to <\$400/kW by 2012. In addition to the use of low-cost cell-separators, the completed preliminary stack design shown in Figure 3 includes several modifications to the previous hardware; (1) an increase in cell active area

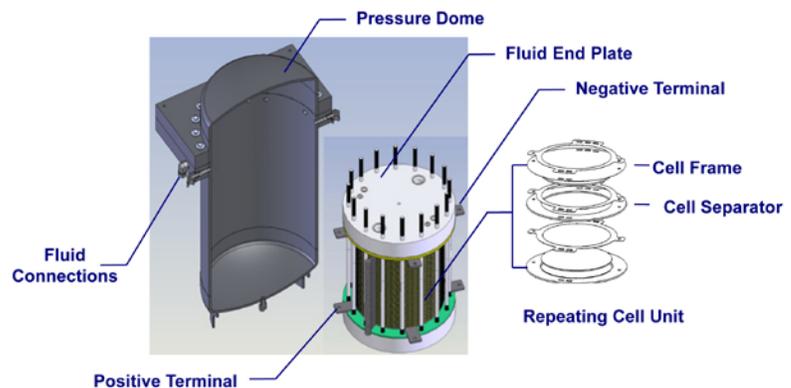


FIGURE 3. Preliminary Stack Design

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 and the materials scrap rate, (2) an overall decrease in parts count per cell (from 41 to 11), (3) a 75% reduction in catalyst loadings, (4) molded thermoplastic cell frames resulting in a cost reduction of 95% for this component alone, and (5) the use of a pressurized dome that encloses the electrolyzer stack to conform to the regulatory code requirements pertinent to hydrogen generators.

Our subcontractor, Parker Hannifin Ltd. (Parker) has completed the preliminary system design which includes the PFD, the P&ID, and the control logic diagrams. The dimension of the electrolyzer system shown in Figure 4 is roughly 6' x 6' x 6.5'. The layout is effectively broken into three zones, namely the oxygen (O₂) compartment, the hydrogen (H₂) compartment, and the controller section. The O₂ compartment contains the oxygen gas-phase separator, a circulating liquid pump, and the deionized water feed tank; the H₂ compartment, encloses the high- and low-pressure hydrogen gas-phase separators, heat exchanger, cooling fans, and various flow valves. The refrigeration unit, a component of the H₂-dryer that is used to cool H₂ gas prior to entering the dryer, is located below the controller and adjacent the electronic power supply. Nitrogen (N₂) tanks provide nitrogen gas for filling the dome and for purging the electrolyzer stack during start-up and shut-down.

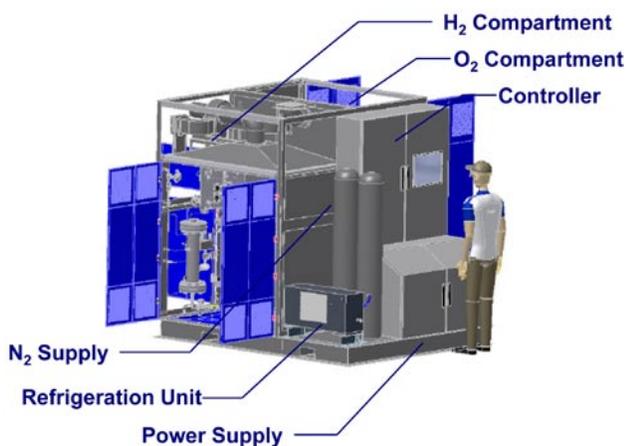


FIGURE 4. Preliminary System Design

Conclusions and Future Directions

Significant progress has been made in DSM™ membrane development. GES has demonstrated membrane reproducibility and durability as well as a significant improvement in electrolyzer cell efficiency that exceeds the DOE's 2017 target. In addition, development efforts conducted under this project have resulted in the reduction in the cost of the moderate-pressure PEM-based electrolyzer systems, an increase in the life of the low-cost cell-separators, and improved balance-of-plant components efficiency. The future objectives (by company) are to:

- Parker Hannifin
 - Continue fabrication and evaluation of key system components
 - Complete critical design review
 - Fabricate and operate deliverable system
- GES
 - Fabricate scaled-up 'short stack' prototype (0.1 kg-H₂/hr)
 - Scale-up DSM™ (to 290-cm²)
 - Scale-up Cell-Separators (to 290-cm²)
 - Operate short stacks at GES for 1,000 hours
 - Assist in system start-up at Parker facilities
 - Receive and install operating system at GES
 - Add cells to stack to increase capacity to 0.5 kg-H₂/hr
 - Verify stack/system performance
 - Demonstrate prototype system at NREL
- Virginia Polytechnic Institute
 - Complete fabrication of alternative hydrocarbon membrane
 - Evaluate 100-hour durability

FY 2010 Publications/Presentations

1. M. Hamdan, *PEM Electrolyzer Incorporating an Advanced Low-Cost Membrane*. 2010 Hydrogen Annual Program Merit Review Meeting. Presentation #pd_030_hamdan, June 10, 2010.

References

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