2012 Hydrogen Program

Annual Merit Review Meeting

# PEM Electrolyzer Incorporating an Advanced Low Cost Membrane

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Project ID# PD030

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**In 2011 Giner Electrochemical Systems, LLC merged into Giner, Inc.**

# Overview

## Timeline

- **Project Start:** May 2008
- **Project End:** April 2012
- **Percent Complete:** 90

## Budget

- **Total Project Budget: $2.49MM**
  - **DOE Share:** $1.99MM
  - **Contractor Share:** $0.51MM
  - **Funding Received in FY11:** $280K
  - **Planned Funding (FY12):** $278K

## Barriers

**Hydrogen Generation by Water Electrolysis**

- **G. Capital Cost**
- **H. System Efficiency**

## Technical Targets: Distributed Forecourt Water Electrolysis[1]

| Characteristics | Units | 2006 Status | 2015 | 2017 | GES Status (2012) |
|---|---|---|---|---|---|
| Hydrogen Levelized Cost[2] | $/kg-$H_2$ | 4.20 | 3.30 | <2.70 | 3.64 |
| Electrolyzer Cap. Cost | $/kg-$H_2$ | 1.20 | 0.70 | 0.30 | 0.60[3] (1.06)[4] |
| System<br>Electrolyzer Efficiency | %LHV<br>%HHV | 62<br>(73) | 69<br>(82) | 74<br>(87) | System Under Evaluation[5] |

[1] 2007-2009 MYRDD Plan, Electricity cost of $0.04/kW. [2]Production Only (No CSD. CSD costs are expected to add $2.00/kg). [3] Stack Only. [4] Overall system (Stack & BOP). [5]Stack efficiency measured at 74%LHV (87% HHV)

## Partners

- **Parker Hannifin Corporation (Industry)**– System Development
- **Virginia Tech University (Academic)**– Membrane Development

## Collaborations

- **3M Fuel Cell Components Program**– NSTF Catalyst & Membrane
- **Entegris** – Carbon Cell-Separators
- **TreadStone Technologies** – Metal Cell-Separators
- **Tokuyama** – Low-Cost Membrane
- **Prof. R. Zalosh (WPI)** – Hydrogen Safety Codes

# Relevance: Project Objectives

### *Overall Project Objectives*

- Develop and demonstrate advanced low-cost, moderate-pressure PEM 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 & system

### *Relevance*

- Successful development of a low-cost hydrogen generator will enable
  - Early adoption of fuel cell vehicles
  - Integration of renewable energy sources

### *FY 2011-12 Objectives*

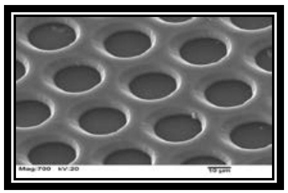
- Complete electrolyzer stack & system assembly
- Evaluate electrolyzer performance & efficiency
- Deliver and demonstrate prototype electrolyzer system at NREL

***Low-Cost PEM Electrolyzer Stack***

# Approach: Overview

## Membrane

- Develop High-Strength, High-efficiency membranes



**DSM**

- DSM-PFSA ionomer incorporated in an engineering plastic support
- Investigate Alternative Low-Cost Membranes
  - Hydrocarbons ionomers
  - Bi-Phenyl Sulfone (VT)
  - PFSA (850EW) membrane (3M)

## Cell-Separator

- Develop cell-separators with
  - High electrical conductivity
  - Resistant to hydrogen embrittlement
  - Stable in oxidizing environment
  - Low-Cost

- Evaluate methods of bonding dissimilar metal films
- Evaluate non-metal substrate with conductive coating

**2011-2012:** Investigate alternative Mat'l & technologies for future cost reductions. Includes: nitrided components, low-cost carbon (Entegris), and TreadStone cell-separators

## Electrolyzer Stack

- Reduce parts count/cell
- Develop innovative designs to reduce Mat'l costs
- Apply manufacturing methods to reduce costs
- Increase active cell areas
- Fabricate 0.5kg-$H_2$/hr Stack utilizing low-cost components

**2011-2012:** Design & develop high pressure stack designs

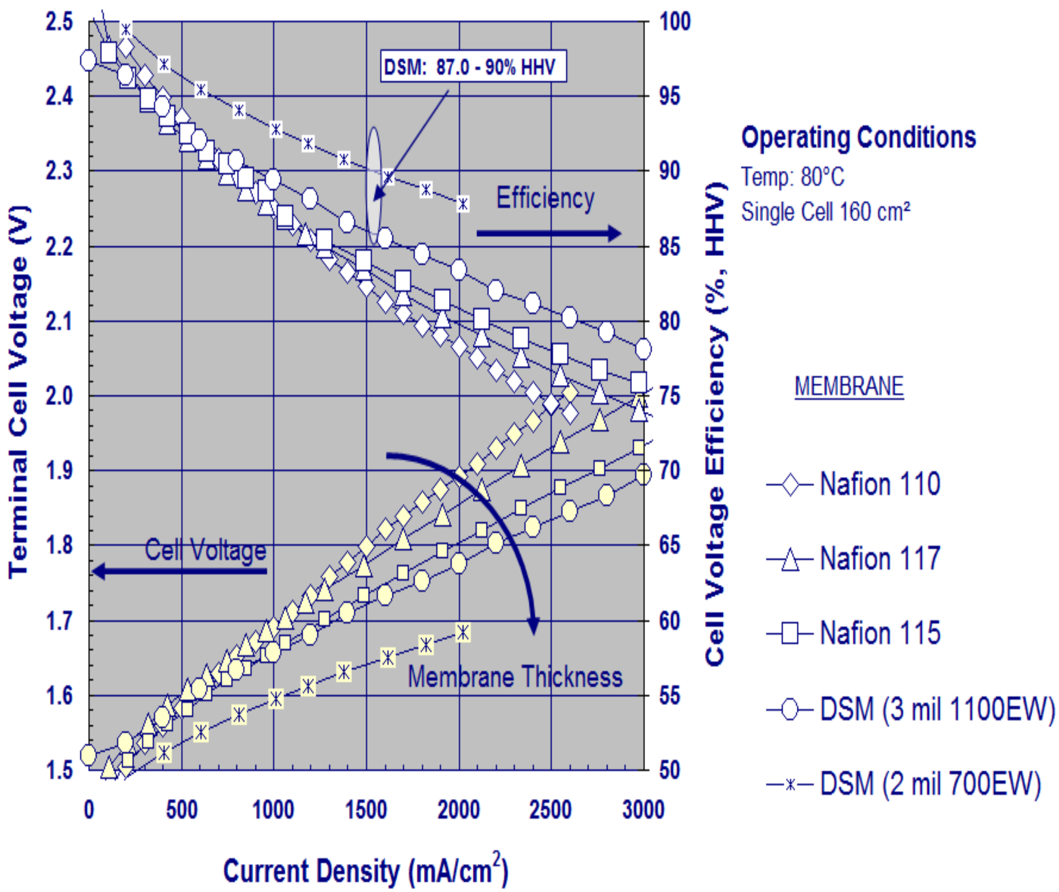
## Electrolyzer System

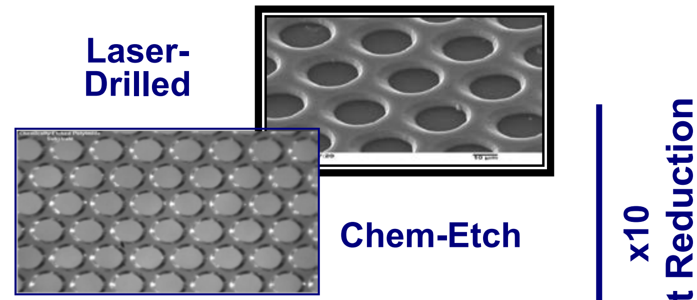
- Reduce BOP capital cost
- Reduce BOP power consumption-through higher efficiency power electronics
- Design & test high efficiency $H_2$ dryer
- Improve safety and reliability
- Design for high-volume manufacturing
- Team with large volume commercial manufacturer (**Parker-Hannifin**)

# Approach: 2011-12 Milestones

| | Go/No Go Decision Points | Progress Notes | %Complete |
|---|---|---|---|
| Membrane | ■Scale-up DSM membrane to 290cm² <br> ■Evaluated in short stack @ 80°C and 1500-1700 mA/cm² | ■Operated Scaled-up membrane in 5-cell for 1000-hours; **Single-cell > 5000 hours** <br> ■Use of chemically-etched supports further reducing membrane costs <br> ■Performance DSM > Nafion® 1135 <br> ■Testing indicates low membrane degradation rate, high life expectancy | **100%** (June 2011) |
| Cell Separator | ■Scale-up Carbon/Ti cell-separators to 290-cm² <br> ■ Cell-separators evaluated in short stack @ 80°C and 1500-1700 mA/cm² | ■Operated 290-cm² cell-separators in 5-cell for 1000-hours; **Single-cell > 5000 hours** <br> ■$H_2$-embrittlement testing confirms longevity of Carbon/Titanium cell-separators | **100%** (June 2011) |
| | | ■Continuing investigation of new Mat'l for future cost reductions. Includes: nitrided components, low-cost carbon (Entegris), and TreadStone cell-separators <br> ■ Testing ongoing - over 2000+ hours | **40%** |
| Stack/System Development | ■Completed 27-cell stack assembly and performance evaluations <br> ■Completed fabrication of prototype electrolyzer system capable of providing 12 kg-$H_2$/day at 300-400 psi that has the potential of meeting DOE's 2012 cost target for distributed $H_2$ production of <3.70/kg-$H_2$ | ■Stack fabricated with carbon/Ti cell-separators and DSM in addition to several low cost stack components developed during this program | **100%** (March 2011) |
| | | ■System complete, evaluations ongoing | **100%** (Feb 2012) |
| | | ■Remaining: System delivery to NREL for evaluation | Expected (May 2012) |

# Membrane Progress: DSM

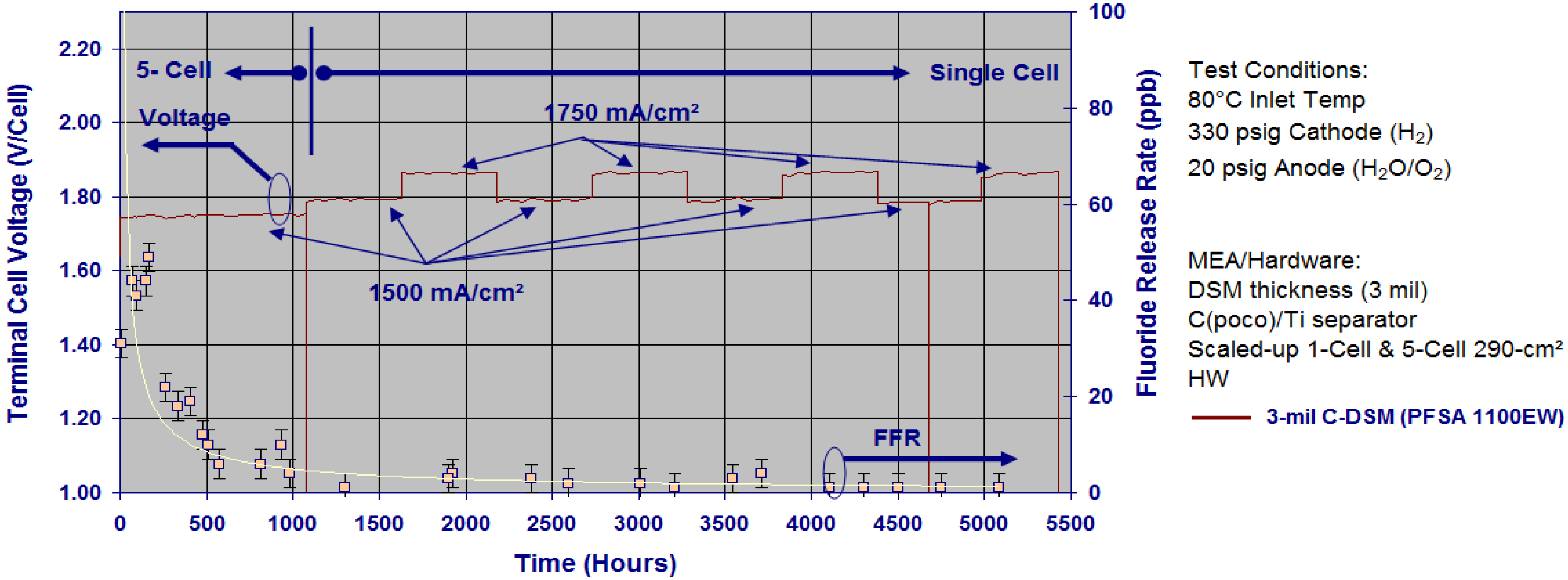



## DSM Supports

- Developed high efficiency DSM membranes
  - Chem-etched substrates used to lower cost, aid ease of fabrication
- Developed electrode structures with reduced catalyst loadings: 0.7 mg Pt/cm² (Pt/Ir-Anode), 0.4 mg Pt/cm² (Pt/carbon-Cathode)
  - Previously 8 mg Pt/cm²
- Successful testing of 3M NSTF Pt (cathode) and PtIr (anode) catalyst: 3M catalysts are one-order magnitude lower (~0.10 to 0.15 mg Pt/cm² Anode/Cathode)
- Alternative hydrocarbon membranes exhibited high degradation rates

# Membrane Progress: 5000 hour Durability Testing




## Performance

- Completed 1000 Hour Life Test Milestones
  - Scaled-up 5-cell (290-cm²)
  - 1.73-1.75V (~88% HHV)
- DSM MEA from 5-cell short stack re-assembled into a single-cell stack, total operating time = 5430 hours
- Scaled-up cells include low-cost components used in final stack assembly

## Membrane Degradation (Estimated Lifetime)

- F ion Release Rate: 3.7 μg/hr (<10 ppb)
- DSM -1100EW (Stabilized Ionomer): ~55,000 hours

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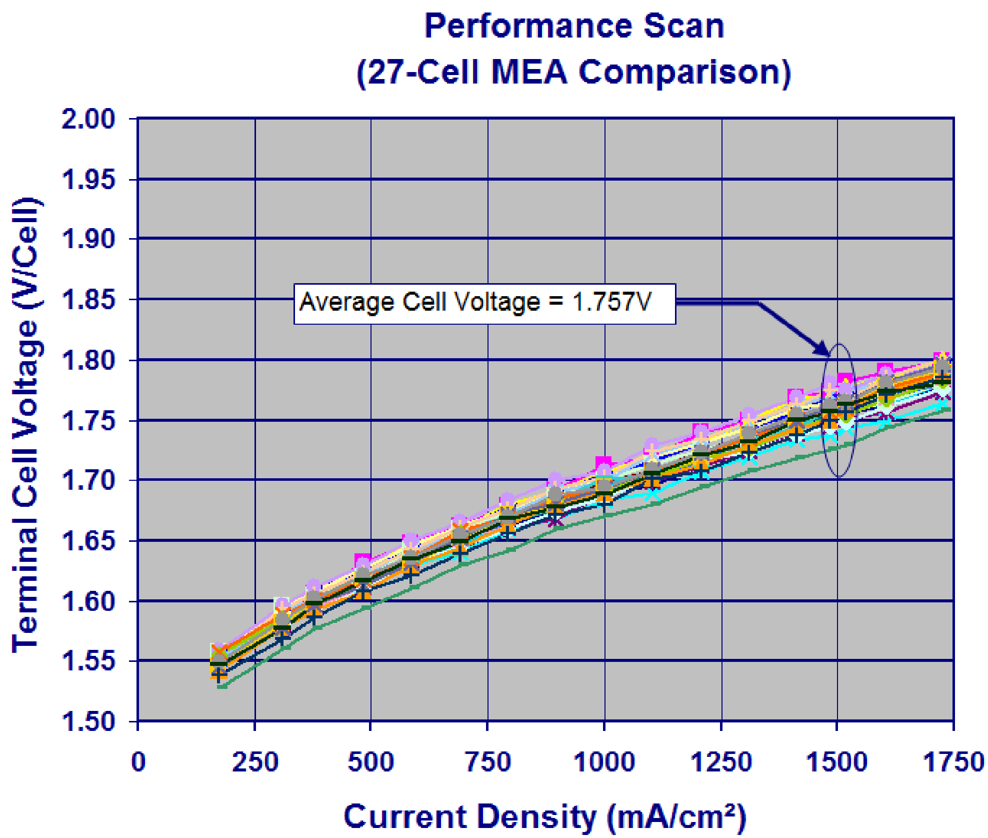
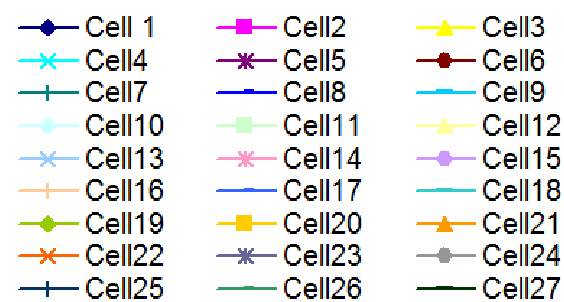
# Membrane Progress: 27-Cell Stack Performance




Test Conditions:
80°C Inlet Temp
330 psig Cathode ($H_2$)
20 psig Anode ($H_2O/O_2$)

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



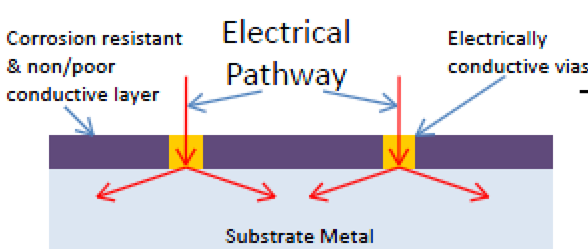

## Stack Performance

- Average cell voltage of 1.757V @ 1500 mA/cm² & 80°C
- High Stack voltage efficiency 87% HHV (73.6% LHV) @ 1500 mA/cm²; Energy efficiencty;46.6 kWh/kg
  - Efficiencies in line with DOE 2015 goals
- Voltage variations due to minor differences in membrane thicknesses

# Cell-Separator Progress

## Carbon/Titanium

- Carbon/Titanium Cell-Separators Scaled-up to 290-cm² (Milestone June-2011)
  - Evaluated in cell short stack for 5000+ hours
  - Cell-Separators fabricated with low porosity carbon
    - POCO Pyrolitic Graphite (Surface Sealed)
- Analysis
    - Low hydrogen uptake (embrittlement)
    - **Life time estimate > 60,000 hours**
- Alternative low-cost materials identified
  - Carbon, Nitrided, & TreadStone Cell-Separators

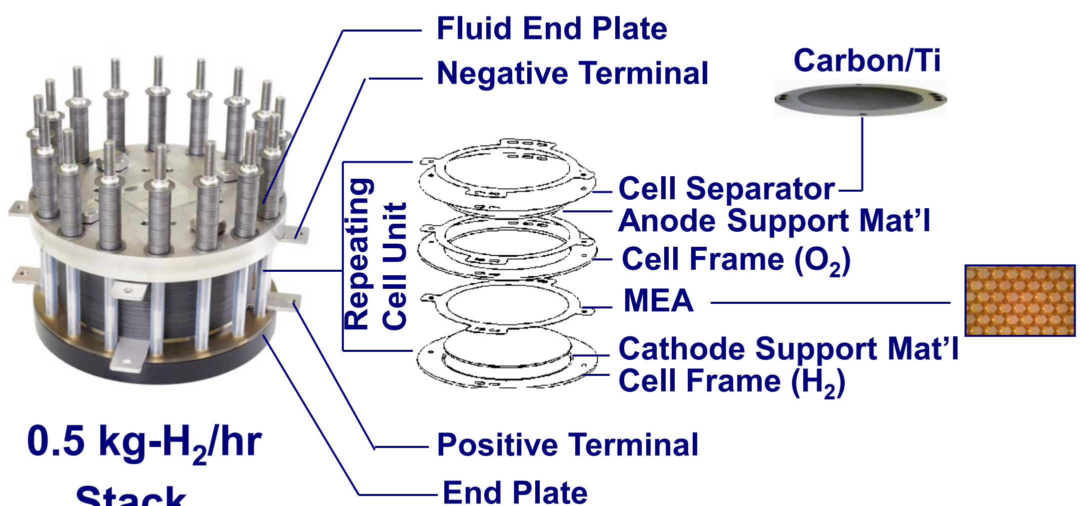



TreadStone's Cell-Separator Design utilizes low-cost base metal substrate

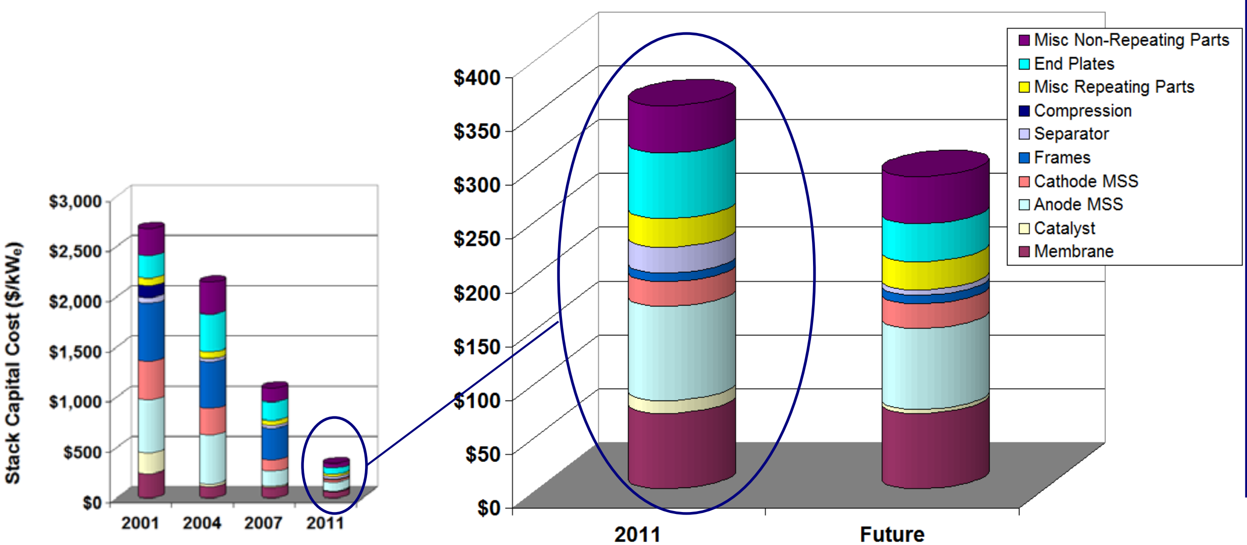
| Cell -Separator | Time (Hours) | $H_2$ uptake (ppm) |
|---|---|---|
| *new* **TreadStone** | **2000+** | **Ongoing** |
| *new* **C/Ti (290-cm²)** | **5430** | **104** |
| **C/Ti (290-cm²)** | 1000 | 105 |
| **C/Ti (160-cm²)** | 500 | 64 |
| **Zr/Ti(160-cm²)** | 500 | 140 |
| **ZrN/Ti (160-cm²)** | 500 | 31 |
| **Dual Layer Ti (160-cm²)** | 500 | 1105 |
| **Ti (baseline)** | 0 | ≈ 60 |
| Ti Failure/Embrittlement: ~8000 ppm | | |

| Property | Units | DOE Target FC Bipolar Plates 2015 | GES C/Ti Cell-Separator 2011 |
|---|---|---|---|
| Cost | \$/kW | 3 | > 10 |
| Weight | kg/kW | <0.4 | 0.08 |
| Electrical Conductivity | S/cm | > 100 | >300 (680 Poco) |
| Flexural Strength | MPa | >25 | 86.1 (Poco) |
| Contact Resistance to GDL | mΩ. cm² | < 20 @ 150 N/cm² | 17 @ 350 N/cm² |

# Stack Progress: Advancements & Cost Reductions




**0.5 kg-$H_2$/hr Stack**




**>60% Cost Reduction in Stack Costs (2007-2011)**

## Stack Improvements

- Increased active area (160->290cm²)
- Reduced catalyst loadings 8->1 mg/cm²
- Reduced Part Count from 41 to 10 Parts/Cell-50% labor reduction
- Pressure Pad: Sub-assembly eliminated
- Molded Thermoplastic Cell Frame
- Cell-Separators: Replaced Nb/Ti with Carbon/Ti
- Frame Thickness reduced (by 30%)
  - Reduces Cathode & Anode Support Mat'l
- DSM MEAs fabricated w/chem-etch supports- 90% cost reduction
- Carbon Steel End Plate (previously S.S.) - 66% material cost reduction

- *The repeating cell unit comprises 90% of electrolyzer stack cost*
- *Labor Content ranges from 33-50% cost of stack (depending on volumes)*
- *Implementing current developments expect to reduce cost to <$300/kW*

# System Progress

- Assembly: 100% Complete
- System Modifications
- Eliminate stack enclosure (Dome) but ensure safety & future method of high-pressure operation
  - Safety
    - Added ventilation fan to satisfy safety Hydrogen Refueling System Safety Codes
    - Stack proof pressure tested to 2x operating pressure
    - Electrical lockout added to stack chamber
  - High-Pressure Operation
    - Initiated fabrication of high-pressure stack design
    - Differential pressure operation
    - Utilizes containment rings
    - 6250 psig pressure test successful
    - Work conducted under DOE program DE-SC0001486 (PD065)

**System Specs**

Dimensions: 7.20′ tall x 6.6′ long x 7.84′ wide.

Water Consumption: 5.75 liters/hr

Stack Power Requirement: 24 kW

Heat rejection: 3.3 kW

**Production Rate**

0.5 kg $H_2$/hr (-3% dryer)

2.0 kg-$H_2$/hr (w/larger Stack & Power Supply)

**Operating Pressure**

$H_2$ 350 psig; $O_2$ atm

**Operating Temperature**

80°C

**Membrane**

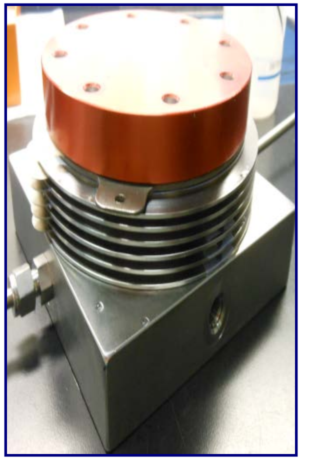
DSM-PFSA,

**Stack Size**

290 cm²/cell, 27 Cells

**Stack Current Density**

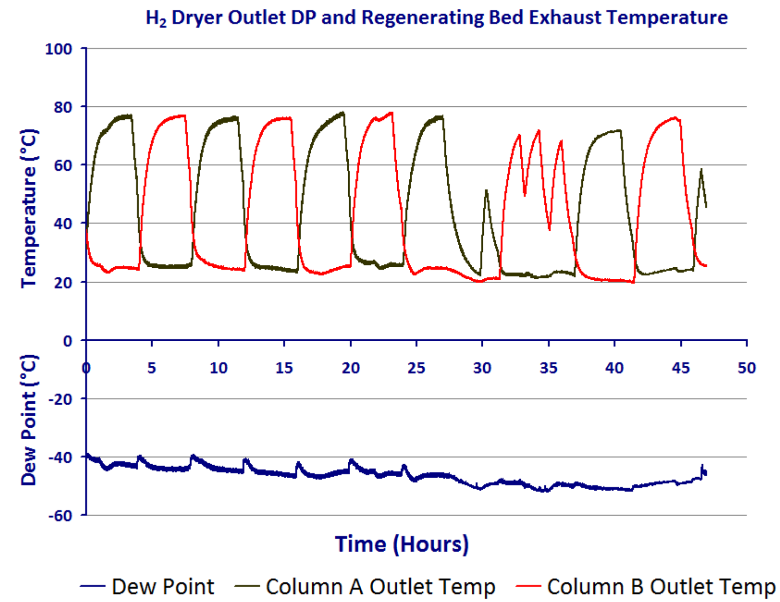
~1750 to 1900 mA/cm²

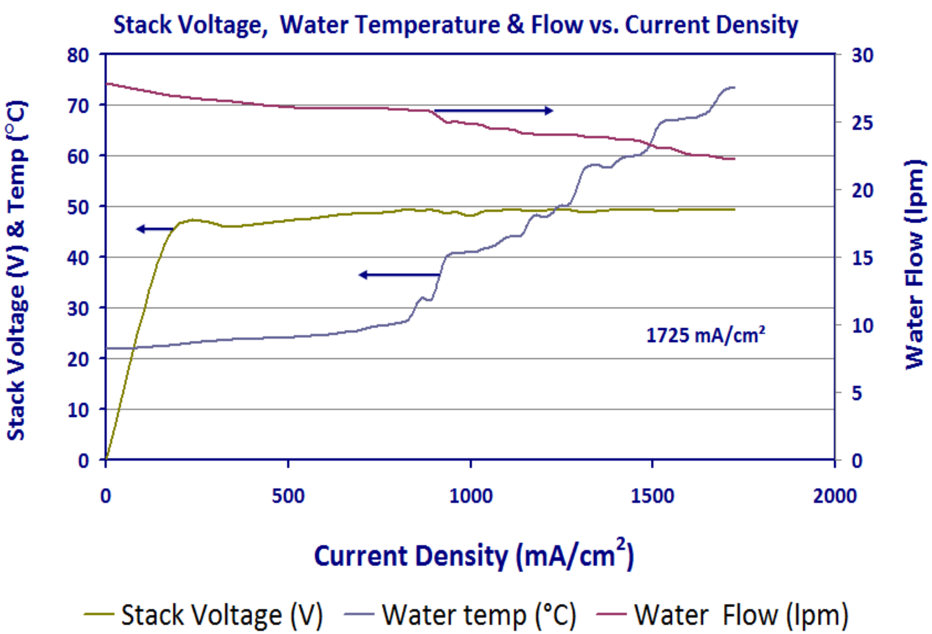


**Future electrolyzer stack designs utilizing containment rings for high pressure operation**

# System Progress: Performance

- Accumulated ~ 100 hours of system operation
  - Constant voltage operation
    - Start-up ~ 1 hour to full temp. & current density
  - Hydrogen Outlet Pressure 300-400 psig
  - Oversized phase-separator to accommodate larger stacks
    - $H_2$ pressure/volume in separator controlled with higher current density operation




- $H_2$-Dryer
  - Dual-desiccant dryer to reduce maintenance and desiccant replacement
    - Achieved $H_2$ outlet dew point of -51°C
    - Optimizing $H_2$-Dryer to achieve -59°C dew point

# System Progress: Efficiency

**Stack Current Density**

| **Hydrogen Production & Losses** | Units | 1500 mA/cm² | 1750 mA/cm² |
|---|---|---|---|
| Stack H2-Production | $kg\text{-}H_2/hr$ | 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 | 1500 mA/cm² | 1750 mA/cm² |
|---|---|---|---|---|
| **Electrolyzer Stack** | | kW | **20.6** | **24.2** |
| DC 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 |
| H2 sensor circuit pump | | | 0.12 | 0.12 |
| **Total Energy Consumption ( No Dryer)** | | | **22.3** | **26.2** |
| $H_2$-Dryer | Chiller (1.4kW Max) | | 0.46 | 0.60 |
| | Heaters A & B | | 0.07 | 0.07 |
| **Total Energy Consumption (w/Dryer)** | | | **22.9** | **26.8** |

| **Overall Efficiencies** | Units | 1500 mA/cm² | 1750 mA/cm² |
|---|---|---|---|
| **Electrolyzer Stack (includes permeation)** | kWh/kg | **46.6** | **46.9** |
| **System ( No Dryer)** | | **50.5** | **50.8** |
| **System ( w/Dryer)** | | **54.0** | **54.2** |

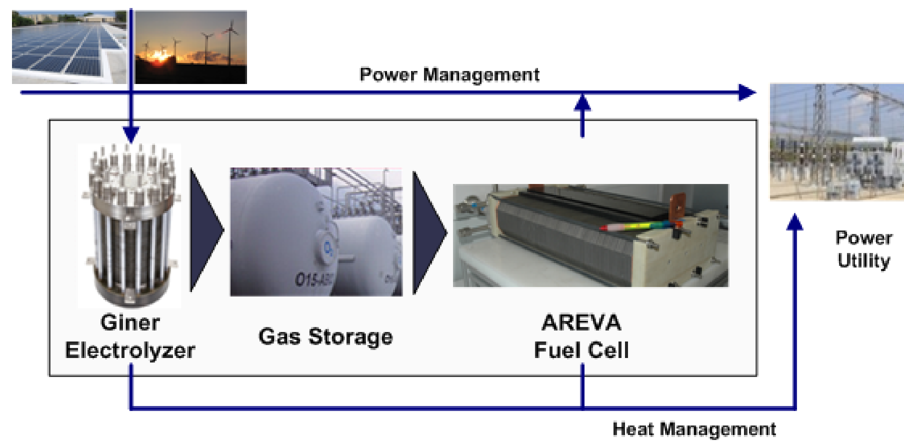
**Preliminary system data during initial 100-hour run**

- Power values based on component ratings and intermittent operation of
- Chiller (compressor)
  - Heater A - on for less than 50% of the dryer cycle. Heater B - as heater A, alternately powered
- Heat exchanger fans A & B
  - Water pump operating less than max rating
- Safety ventilation for indoor operation (+0.7kW)
  - $H_2$ enclosure fan A - running at all times
  - $O_2$ enclosure fan B- running at all times
- Higher efficiencies expected in larger (forecourt & centralized) systems
  - Power Supply – 97%
  - $H_2$ Dryers
- May operate Electrolyzer Stack up to 1900 mA/cm$^2$ to compensate pressure drop in phase-separator (higher $H_2$ production rate)
- Higher efficiencies at lower current densities (higher stack costs)
- System oversized to accommodate larger stacks

# Recent Market Developments

- **Low-cost electrolyzer stack developed during DOE program commercialized and now in-use at Areva Site**
  - Operating at 2 sites
  - Customer confirms 1,000 hours at 47 $kWh_e$/kg
- **Target markets are in-line with DOE goals and include**
  - Intermittent Renewable Energy Source (RES) integration
  - Backup power for grid outages and load shedding
  - Increase RES ratio and ensure grid stabilization
- **Market Drivers**
  - **U.S. National Defense Authorization Act of FY2007/FY2010:**
    - DoD must produce 25% of total energy from renewable energy sources by 2025
  - **European Commission**[1]
    - 2020 Strategy: 20% share of renewable energy in EU energy consumption, with a 10% share in transport
    - 2050 Roadmap calls for a 55 - 75% share of RES in gross final energy consumption


**AREVA's energy storage platform 'GREENERGY BOX' in Corsica, France Utilizing GES Low-Cost Electrolyzer Stack**




**Modular RFC systems with energy storage from 0.2 to 2MWh**

[1]http://ec.europa.eu/energy/energy2020/roadmap/doc/com_2011_8852_en.pd f

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# Projected $H_2$ Cost

| ***Specific Item Cost Calculation*** **Hydrogen Production Cost Contribution** | | | | |
|---|---|---|---|---|
| H2A Model Version (Yr) | | Rev. 2.1.1 (FY2011) | | Rev. 2.1.1 (FY2012) |
| | | | | |
| Capital Costs | Stack | $0.60 | | $0.60 |
| | Balance of Plant | --- | | $0.46* |
| Fixed O&M | | $0.39 | | $0.59* |
| Feedstock Costs $1.54 minimum @ 39.4 $kWh_e/kg\text{-}H_2$ | | $1.86 | | $1.97 (50.5 kWh/kg) |
| Byproduct Credits | | $0.00 | | $0.00 |
| Other Variable Costs (including utilities) | | $0.01 | | $0.01 |
| ***Total Hydrogen Production Cost* ($/kg)** (No CSD) | | **2.86** | | **3.64** |
| Delivery (H2A CSD default) | | 1.80 | | 1.80 |
| *Total Hydrogen Production Cost* ($/kg) | | **4.66** | | **5.43** |

## H2A Model Analysis Forecourt Model

- Design capacity: 1500 kg $H_2$/day
- Assume large scale production- costs for 500th unit
- Assume multiple stacks/unit
  - Low-cost materials and component manufacturing
- 333 psig operation. $H_2$ compressed to 6250 psig
- Operating Capacity Factor: 70%
- Industrial electricity at $0.039/kWh

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- 2012 Total production costs of $3.64/kg
- Progress inline with achieving 2015 Target of $3.30/kg
- *Additional BOP/O&M costs largely due to hydrogen management components (dryer, chiller, …)

# Future Plans for FY2011-12

- Complete investigation on low-cost components
  - Includes Low-cost carbon, nitrided, and TreadStone Cell-separators
- Complete additional ~200 hours system evaluation
  - Optimize operation of system components ($H_2$-Dryer)
- Continue development of high-pressure (5000 psi), low-cost stacks
- Deliver system to NREL for evaluation

## Future Challenges

- Labor is 33-50% cost of stack (depending on volumes)
  - Implementing new manufacturing processes to reduce labor costs
    - Unitize cell components (Further reducing parts/cell)
      - Combine cell components at the production level
        - Anode support Mat'l + Separator + Carbon cathode
        - Frame + gasket, Frame + MEA
    - Investigate techniques to mold to exact dimensions of cell components
    - Improve pressure capabilities of stacks (5000 psi or higher)
    - Increase stack active-area to $1ft^2$ (or larger)
    - Automate stack & MEA assemblies

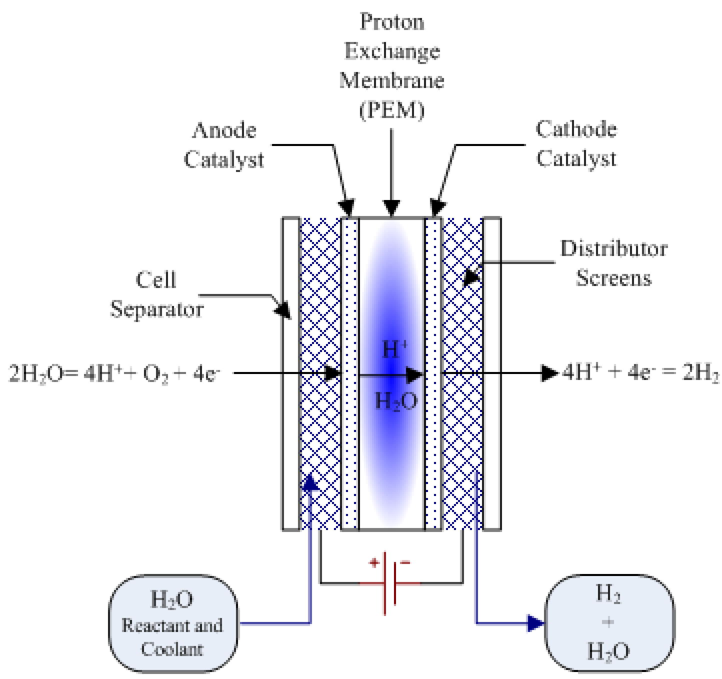
# Summary

- **Membrane: Demonstrated Reproducibility, Durability, and Efficiency**
  - Demonstrated high efficiency DSM membranes (single-cell, 5-cell, and 27-cell stacks)
  - Demonstrated 5000+ hrs lifetime of scaled-up (290 $cm^2$) DSM membrane at 80°C
  - Cell voltage efficiency 87%HHV (@ 1500 $mA/cm^2$) meeting 2015 DOE targets
  - Stack Efficiencies: 46.6 $kWh_e/kg\text{-}H_2$ @ 1500 $mA/cm^2$
- **Cell Separator & Component Development:**
  - Demonstrated 5000+ hrs lifetime of scaled-up cell-separators
  - Demonstrated significantly reduced hydrogen embrittlement with carbon/Ti separators
    - Expected cell-separator lifetime in the range > 60,000 hours
- **Scaled-Up Stack:**
  - Stack assembly 100% complete
  - Significant progress made in stack cost-reduction (cell-components, membrane, & catalyst)
    - 60% reduction in stack cost (from 2007 to 2011)
- **System Development:**
  - System complete, evaluation ongoing
  - Delivery to NREL expected in May 2012

# AMR
# Technical Slides

# Technical Slide 1-

## Technical principle of the PEM-based water electrolysis




### PEM Cell Reactions

| | |
|---|---|
| $H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2$ | Anode half-cell reaction |
| $2H^+ + 2e^- \rightarrow H_2$ | Cathode half-cell reaction |
| $H_2O + 2e^- \rightarrow H_2 + \frac{1}{2}O_2$ | Overall reaction |

### Water permeation through PEM

$\sim 3H_2O/H+$

# Technical Slide 2- Efficiency

## Power Efficiency

The dissociation of 1 mole of liquid water to produce a mole of hydrogen at 25°C requires 285.8 kJ of energy. The conversions made below show the HHV in terms of kWh/kg from 285,840 Joules per mole (J/mole);

$$285{,}840\frac{J}{\text{mol}} * \frac{1\text{mol H}_2}{2.0158\text{ g}} * \frac{1000g}{1kg} = 141{,}799{,}781\frac{J}{kg} = 141.8\frac{MJ}{kg}$$

$$141.8\frac{MJ}{kg} * \frac{1\text{watt}-\text{sec}}{J} * \frac{1kW}{1000w} * \frac{1hr}{3600\text{sec}} = 39.4\frac{kWh}{kg} \quad (100\%, HHV)$$

## Voltage Efficiency

$$E_o = \frac{\Delta_f H^\circ}{zF} = \frac{285{,}840\frac{J}{mol}}{2 * 96{,}485\frac{C}{mol}} = 1.48 \frac{Volts}{cell}$$

The Nernst potential (Vn) adds an additional term to the standard potential (EO) to account for the electrochemical compression energy required to pressurize the gases in the stack.

$$V_n = E_O + \frac{RT}{nF}\ln\left(\frac{P_{H_2}P_{O_2}^{\frac{1}{2}}}{P_{H_2O}}\right)$$

@ 27 atm and 80°C

$$V_n = 1.48 + \frac{8.341(353)}{2(96485)}\ln\left(\frac{(27)\sqrt{1.3}}{1.3}\right) = 1.48 + 0.048 = 1.528\ V$$

$$\text{Stack Efficiency} = \frac{\text{Ideal Stack Potential}}{\text{Actual Stack Potential}} = \frac{1.528}{1.757}(100) = 87\%(HHV)$$

## Hydrogen Production (Current Efficiency)

The theoretical rate of hydrogen production in an electrolyzer stack for 1 Amp load;
$dN/dt = i/n\mathcal{F} = 1A/(2e^- * 96487C/mole) = 5.18 \times 10^{-6}$ mol $H_2$/sec.
From the ideal gas law at STP (273K,1 atm)
$V_{H2} = nRT/P = (5.18 \times 10^{-6}$ mol $H_2$/sec) x (60s/min)x(1000cm$^3$/L) x (0.0821L.atm.mol-1.K-1) = **6.96 cm³/min** ($H_2$ per Amp)

Losses of $H_2$ production (faradaic inefficiencies) are indicative of gas permeation through membrane. Dependent on membrane thickness and pressure;