II.0 Hydrogen Production Program Overview

INTRODUCTION

The Hydrogen Production program supports research and development (R&D) of technologies that will enable the long-term viability of hydrogen as an energy carrier for a diverse range of end-use applications including stationary power (e.g., backup power and combined heat and power systems), transportation (e.g., specialty vehicles, cars, trucks, and buses), and portable power. A portfolio of hydrogen production technology pathways utilizing a variety of renewable energy sources and renewable feedstocks is being developed under this program.

Multiple DOE offices are engaged in R&D relevant to hydrogen production, including:

- The Fuel Cell Technologies Office (FCTO), within the Office of Energy Efficiency and Renewable Energy (EERE), is developing technologies for distributed and centralized renewable production of hydrogen. Distributed production options under development include reforming of bio-derived renewable liquids and electrolysis of water. Centralized renewable production options include water electrolysis integrated with renewable power generation (e.g., wind, solar, hydroelectric, and geothermal power), biomass gasification, solar-driven high-temperature thermochemical water splitting, direct photoelectrochemical water splitting, and biological processes.
- The Office of Fossil Energy (FE) is advancing the technologies needed to produce hydrogen from coal-derived synthesis gas, including co-production of hydrogen and electricity. Separate from the Hydrogen and Fuel Cells Program, FE is also developing technologies for carbon capture, utilization, and storage, which will ultimately enable hydrogen production from coal to be a near-zero-emissions pathway.
- The Office of Science's Basic Energy Sciences program conducts research to expand the fundamental understanding of biological and biomimetic hydrogen production, photoelectrochemical water splitting, catalysis, and membranes for gas separation.
- The Office of Nuclear Energy (NE) has been conducting efforts in the development of high-temperature electrolysis, under the Next Generation Nuclear Plant (NGNP) project, which also includes evaluations of other end-user applications and energy transport systems. The previous activity, the Nuclear Hydrogen Initiative, was discontinued in Fiscal Year (FY) 2009 after steam electrolysis was chosen as the hydrogen production pathway most compatible with the NGNP.

GOAL

The goal of the Hydrogen Production program is to develop low-cost, highly efficient hydrogen production technologies that utilize diverse domestic sources of energy, including renewable resources (EERE), coal with sequestration (FE), and nuclear power (NE).

OBJECTIVES[1]

The objective of the Hydrogen Production program is to reduce the cost of hydrogen dispensed at the pump to a cost that is competitive on a cents-per-mile basis with competing vehicle technologies. Based on current analysis, this translates to a hydrogen threshold cost of $2–$4 per gallon gasoline equivalent (gge) (produced, delivered and dispensed, but untaxed) by 2020[2], apportioned to $1-$2/gge for production only[3]. Technologies are being developed to achieve this goal in timeframes appropriate to their current stages of development.

The objectives of FE's efforts in hydrogen production are documented in the *Hydrogen from Coal Program Research, Development and Demonstration Plan* (September 2010)[4]. They include proving the feasibility of a near-zero emissions, high-efficiency plant that will produce both hydrogen and electricity from coal and reduce the cost

[1] Note: Targets and milestones were recently revised; therefore, individual project progress reports may reference prior targets.
[2] Hydrogen Threshold Cost Calculation, Program Record (Office of Fuel Cell Technologies) 11007, US Department of Energy, 2012, http://www.hydrogen.energy.gov/pdfs/11007_h2_threshold_costs.pdf
[3] *Hydrogen Production and Delivery Cost Apportionment*, Program Record (Office of Fuel Cell Technologies) 12001), US Department of Energy, 2012
[4] *Hydrogen from Coal Program Research Development and Demonstration Plan*, Office of Fossil Energy, US Department of Energy, September 2010, http://fossil.energy.gov/programs/fuels/hydrogen/2010_Draft_H2fromCoal_RDD_final.pdf

of hydrogen from coal by 25 percent compared with current technology by 2016. The objectives of NE's efforts in hydrogen production are documented in the *Technology Roadmap for Generation IV Nuclear Energy Systems* (December 2002)[5]. They include the development of high-temperature thermochemical process for hydrogen production compatible with NGNP.

FY 2013 TECHNOLOGY STATUS AND PROGRESS

In FY 2013, significant progress was made by the Hydrogen Production program on several important fronts. For example:

- The Hydrogen Production Expert Panel (HPEP), a Hydrogen and Fuel Cell Technical Advisory Committee (HTAC) subcommittee collected input from experts from industry, academia, and national laboratories during a May 2012 workshop and developed recommendations based on that input. HPEP was tasked with providing recommendations to enable the widespread production of affordable, low-carbon hydrogen to HTAC, which was established under Section 807 of the Energy Policy Act of 2005 to provide technical and programmatic advice to the Energy Secretary on DOE's hydrogen research, development, and demonstration efforts. Key findings were included in the final report that is posted online[6] and are summarized in the next section.
- The Hydrogen Production program's chapter of the *Multi-Year Research, Development and Demonstration Plan (MYRD&DP)* was updated. Cost and performance targets for the hydrogen production pathways were identified based on new and updated Hydrogen Analysis (H2Av3) Model production pathway case studies.
- A Memorandum of Understanding with the National Science Foundation was signed allowing for joint funding of RD&D with the FCTO.
- The Hydrogen Production Roadmap was revised and updated by the U.S. DRIVE Hydrogen Production Technology Team.
- The DOE Photoelectrochemical Hydrogen Production Working Group published the Springer Brief in Energy: "Photoelectrochemical Water Splitting: Standards, Experimental Methods, and Protocols."[7]
- The Biological Hydrogen Production Workshop (September 2013) was held to identify key R&D needs.
- A funding opportunity announcement for hydrogen production pathways analysis was released and a new award was made to a team led by Strategic Analysis Inc.

Hydrogen Production Expert Panel Report

An HPEP, comprised of world leaders in hydrogen production technologies from industry, academia and the national laboratories, was established in 2012 as a subcommittee of HTAC. A workshop was held by the panel in May 2012 to formulate recommendations to HTAC about enabling pathways to the widespread production of affordable low carbon hydrogen, both for near- and long-term markets. A summary report resulting from the workshop has been completed and published by HTAC. Key recommendations from the report included: 1) providing incentives to accelerate the production of hydrogen for transportation applications with a particular focus on the steam reforming of natural gas, leveraging this abundant and low-cost domestic resource; 2) considering significant investments in hydrogen production and storage analyses and demonstrations; 3) developing a cohesive plan for all pertinent R&D programs to provide consistent and long-term guidance; and 4) establishing public-private partnerships and/or clusters to create well-defined plans for infrastructure roll-out, establishing appropriate incentives, and promoting uniform codes, standards, and safety regulations.

Production Cost Status and Targets

The status and targets for the projected cost of hydrogen production based on the pathway-specific H2Av3 case studies completed in FY 2013 are shown in Table 1. The technoeconomic assumptions used in these case studies can be found online for each pathway at http://www.hydrogen.energy.gov/h2a_production; and these cases are also fully documented in the new DOE-FCTO MYRD&DP. Targets for hydrogen production efforts in FE and NE (not included

[5] *A Technology Roadmap for Generation IV Nuclear Energy Systems*, Office of Nuclear Energy, US Department of Energy, December 2002, http://www.ne.doe.gov/genIV/documents/gen_iv_roadmap.pdf

[6] Report of the Hydrogen Production Expert Panel (a subcommittee of HTAC), May 2013, http://www.hydrogen.energy.gov/advisory_htac.html

[7] *Springer Brief in Energy*, September 2013, http://link.springer.com/book/10.1007/978-1-4614-8298-7/page/1

in Table 1), along with information on the status of the technologies, are described separately in the previously cited RD&D and roadmap documents for these programs.

TABLE 1. Cost Status and Targets for Hydrogen Production*

	$/gge (production costs only)	Current Status**	2015 Target	2020 Target	Ultimate Production Target
Distributed	Electrolysis from grid electricity	$4.20	$3.90	$2.30	$1-$2
	Bio-derived Liquids (based on ethanol reforming case)	$6.60	$5.90	$2.30	
Central	Electrolysis From renewable electricity	$4.10	$3.00	$2.00	
	Biomass Gasification	$2.20	$2.10	$2.00	
	Solar Thermochemical	NA	$14.80	$3.70	
	Photoelectrochemical	NA	$17.30	$5.70	
	Biological	NA	NA	$9.20	

*H2A v3 technoeconomic assumptions used in the projected cost status and targets for hydrogen production are consistent with the DOE-FCTO MYRD&DP; Apportionment of threshold cost: $1-$2/gge for production, $1-$2/gge for delivery is addressed in FCTO Program record #12001; new H2A v3 case studies are published at http://www.hydrogen.energy.gov/h2a_production.
** Current status as of 2011.
NA - not applicable

Reductions in the projected costs for hydrogen production in several of the nearer term pathways have been realized through continued technical progress in these technologies, as illustrated in Figure 1. Specific technical progress achieved in FY 2013 in both the nearer- and longer-term hydrogen production pathways is addressed in the following sections.

Separation Processes

Membrane separations RD&D continued through the Small Business Innovation Research (SBIR) program and FE. Technical progress included:

- Developed, through a Phase III SBIR project, a sorbent bed to operate downstream of a bulk desulfurization system as a polishing bed to provide an essentially sulfur-free biogas to a solid oxide fuel cell (SOFC). Laboratory testing of a SOFC module running on bio-gas, integration of a clean-up system and power generation module with the SOFC, and initiation of slipstream demonstrations for an integrated SOFC system was completed. The sorbent achieved 17.5 wt% sulfur capacity, with the potential for 2X higher capacity than current commercially available sorbents. (TDA Research, Inc.)
- Continued FE funding for comprehensive engineering design of advanced Pd and Pd-alloy composite membrane separations for hydrogen production from syngas derived from coal or a coal-biomass mixtures. Five membrane projects successfully designed, constructed, and tested membranes with operating gasifier and/or simulated syngas mixtures that produced 2 pounds per day (lb/day) of hydrogen. A down-select process has resulted in two project teams going forward to complete their designs and construct membrane separation modules with the capacity to produce up to 50 lbs/day of H_2. (FE)

Bio-Derived Liquid Pathways

Projects in this area addressed hydrogen production through catalytic steam reforming of pyrolysis oil and aqueous phase reforming of pyrolysis oil at moderate temperatures. Technical progress included:

- Compared hydrogen production by autothermal reforming of pyrolysis oils for three bio-oils feedstocks (oak, poplar, and pine) and demonstrated that the composition of bio-oil has a significant impact on the yield of hydrogen. The highest hydrogen yields were obtained from the poplar bio-oil (11 g H_2/100 gr bio-oil) with a process energy efficiency (70.8%) and projected high-volume cost ($4.26/gge hydrogen) exceeding the 2015 targets of 70%, and $5.90/gge, respectively. (National Renewable Energy Laboratory, NREL)
- Identified a promising pathway, using a WO_3/AL2O_3 + Ru/C catalyst system, for hydrogen production from cellulose through a two-step process: production of ethylene glycol and then short chain polyols, followed by conversion of polyols to H_2 and CO_2 via aqueous phase reforming. Demonstrated >40% ethylene glycol yield by catalytic deconstruction of cellulose in reactor tests. (Pacific Northwest National Laboratory)

Projected High-Volume Cost of Hydrogen for Near-Term Production Pathways

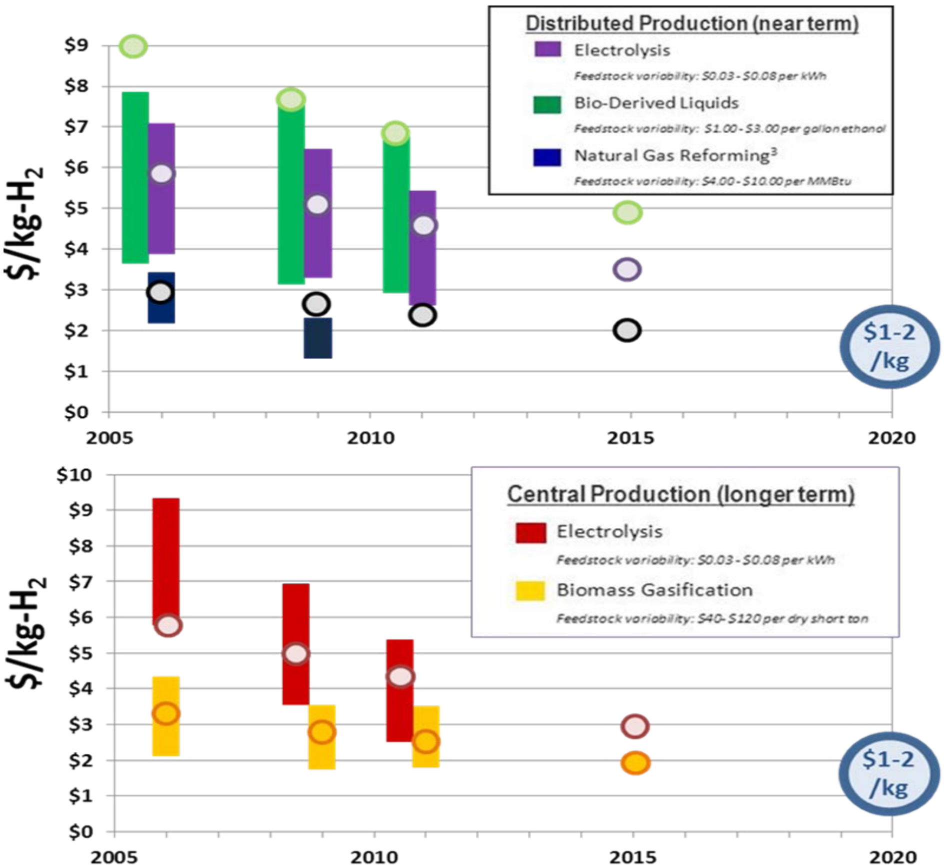


FIGURE 1. HYDROGEN PRODUCTION COST STATUS. Significant progress has been made in several hydrogen production pathways. The hydrogen threshold cost represents the cost at which hydrogen fuel cell electric vehicles are projected to become competitive on a cost-per-mile basis with competing vehicles (gasoline hybrid-electric vehicles) in 2020. Notes: (i) Costs shown do not include taxes. Costs of forecourt compression, storage, and dispensing are not included for distributed technologies, and plant-gate production costs (not including transportation, compression, storage, and dispensing) are shown for centralized technologies. Projections of distributed costs assume station capacities of 1,500 kg/day. Projections of centralized production costs assume capacities of ≥50,000 kg/day. Cost ranges for each pathway are shown in 2007 dollars, based on high-volume projections from H2A analyses, reflecting variability in major feedstock pricing and a bounded range for capital cost estimates. (ii) DOE funding of natural gas reforming projects was completed in 2009 due to achievement of the threshold cost. Incremental improvements will continue to be made by industry.

Electrolysis Hydrogen Production

The major emphases of the electrolysis projects were on cost reduction and efficiency improvement through cell and stack optimization, and validation of integration with renewable resources. Technical progress included:

- Reduced electrolyzer stack costs by 60% compared to a 2007 baseline through low-cost component development resulting in commercial electrolyzer stack products in 30, 60, and 100 cell configurations. (Giner)
- Operated proton exchange membrane (PEM) electrolyzer stacks for greater than 10,000 hours with variable wind profile. Preliminary results indicate no substantial difference in the decay rates between stacks operating under variable wind power versus operating under constant power. (NREL)
- Scaled up and validated advanced stack design with a cell active area of >500 cm^2 and demonstrated single-cell stack prototype operation. Validated a >40% stack cost reduction versus the original project baseline design. (Proton OnSite)

- Demonstrated feasibility to reach <10% catalyst loadings with nanostructured thin film electrodes on multiple membrane types without loss of performance versus baseline electrodes. (Proton OnSite)

Photoelectrochemical (PEC) Hydrogen Production

The broad focus of projects in this area was on utilizing state-of-the-art theory, synthesis, and characterization tools to develop viable PEC material systems and prototypes with improved efficiency and durability. Technical progress included:

- Durability tested multiple surface-treated tandem $GaInP_2$/GaAs electrodes under bias and demonstrated numerous samples which lasted for over a hundred hours with little sign of physical degradation or loss of performance. (NREL)
- Completed quantum molecular dynamics simulations of water electrode interfaces (GaP/InP), and formulated models of interfacial water and wetted surfaces. (Lawrence Livermore National Laboratory, LLNL)
- Applied the innovative model of PEC electrodes developed in 2012 based on the Hamiltonian approach to an unconventional photoelectrode, MoS_2, and submitted results for publication. (LLNL/Stanford)
- Experimentally validated hole-trapping corrosion mechanisms key to stability of PEC devices. (LLNL, in collaboration with the NREL Surface Validation Team)
- Achieved 500 hr durability at 4.1 mA/cm^2 (~5% solar-to-hydrogen efficiency) in a low-cost thin-film silicon-based device. (MVSystems, Inc.)
- Successfully demonstrated bandgap engineering of copper chalcopyrite thin film materials optimized for PEC applications. (MV Systems, Inc., University of Hawaii)
- Successfully demonstrated roll-to-roll production for depositing cobalt oxide films on large area amorphous silicon cells for PEC applications. (Midwest Optoelectronics, LLC)

Biological Hydrogen Production

The broad focus of the projects in the biological hydrogen production portfolio were to address key barriers such as oxygen sensitivity and feedstock utilization using molecular biology and genetic engineering techniques along with improved systems engineering. Technical progress included:

- Demonstrated 10-fold improvement in oxygen tolerance in preliminary experiments in a strain of algae carrying the bacterial Ca1 hydrogenase, which produced hydrogen photobiologically at oxygen concentrations equivalent to 80% of air, at least double the concentration that the native wild-type could tolerate, in the first *in vivo* demonstration of increased oxygen-tolerance of light-driven biological hydrogen production from intact cells. (NREL)
- Developed genetic tools to generate mutants in *Clostridium thermocellum*, and used them to knock out the pyruvate-to-formate reaction pathway that competes for substrates with the hydrogen production pathway, reducing formate production to below detectable levels. (NREL)
- Inserted new promoters for the recombinant Casa Bonita strain hydrogenase genes, which code for the hydrogen-producing machinery, increasing cells' production of the hydrogenase proteins by 16- to 44-fold. (NREL)
- Increased the hydrogen evolution rate of a recombinant, more oxygen-tolerant hydrogenase in the cyanobacteria *Synechococcus elongates* 35-fold through directed mutations of the hydrogenase protein and improvements in maturation gene expression. This new strain has nearly double the hydrogen evolution rate than that of the wild type. (J. Craig Venter Institute)
- Identified the gene mutation that increases *Chlamydomonas reinhardtii* light utilization from the wild-type baseline of 3% to 25% as coding a signal recognition protein, and characterized the role of the protein in light harvesting complex assembly in *C. reinhardtii*. (University of California, Berkeley)

Solar-Thermochemical Hydrogen (STCH) Production

Efforts in these projects were directed toward novel materials design and performance characterization for water splitting by non-volatile metal-oxide-based materials for the high-temperature cycles. For the hybrid cycles with electrolysis steps, efforts were directed toward development of membranes and catalysts for improved performance and durability during the electrolysis step. Technical progress included:

- Demonstrated unchanged current density and voltage characteristics in small 5 cm^2 CuCl electrolyzer cell after Pt loadings were reduced to less than half of the original value, i.e., down from 0.8 mg/cm^2 on both electrodes to 0.4 mg/cm^2 on the cathode and 0.1 mg/cm^2 on the anode. (Argonne National Laboratory)
- Demonstrated long-term stability of the complete electrochemical system for the Sulfur Ammonia (SA) thermochemical reaction cycle, including a greater than 500-hour durability test; and new membranes for the electrolytic cell were identified with up to 2 orders of magnitude lower sulfite flux. A phase-change thermal-storage system concept based on melting and solidification of NaCl was developed to allow for 24/7 operation of the SA cycle. (Science Applications International Corporation, SAIC)
- Discovered a perovskite structure that produces 9x more hydrogen, at a 250°C lower reduction temperature than CeO_2 (1,350°C vs. 1,500°C), the current state-of-the art metal-oxide redox material. H2Av3 analysis of a dish-based H_2 production plant (with SAIC) showed the major contributors to capital cost to be 1) the solar to hydrogen conversion ratio, 2) collector cost, 3) the solar reactor/receiver cost, and 4) electrical power generation cost. (Sandia National Laboratories)
- Isothermal redox at 1,350°C was shown to be feasible for the hercynite cyle with >3x and >12x the production capacity per mass of active material observed than for hercynite and ceria, respectively, during temperature swing water splitting (reduced at 1,350°C and reoxidized at 1,000°C). Results were recently published in *Science*[8]. (University of Colorado, Boulder)
- Modified a Pressurized Button Cell Test Facility, for operation up to 130°C and 1 MPa, for the testing of advanced membranes to reduce polarization losses and SO_2 crossover fluxes for the electrolysis step of the hybrid sulfur reaction cycle was initiated. Candidate anode electrocatalysts, including Pt,Au, PtAu, PtAg, PtPd, AuPd, AuAg, PtCr, and AuCr, that have potential to reduce anode polarization by greater than 100 mV versus state-of-art Pt catalyst, were identified. (Savannah River National Laboratory)

Analysis

The focus of the analysis efforts were on the development of standardized procedures for formulating hydrogen pathway case studies utilizing the H2Av3 tool with technical inputs from production pathway experts. Technical accomplishments included:

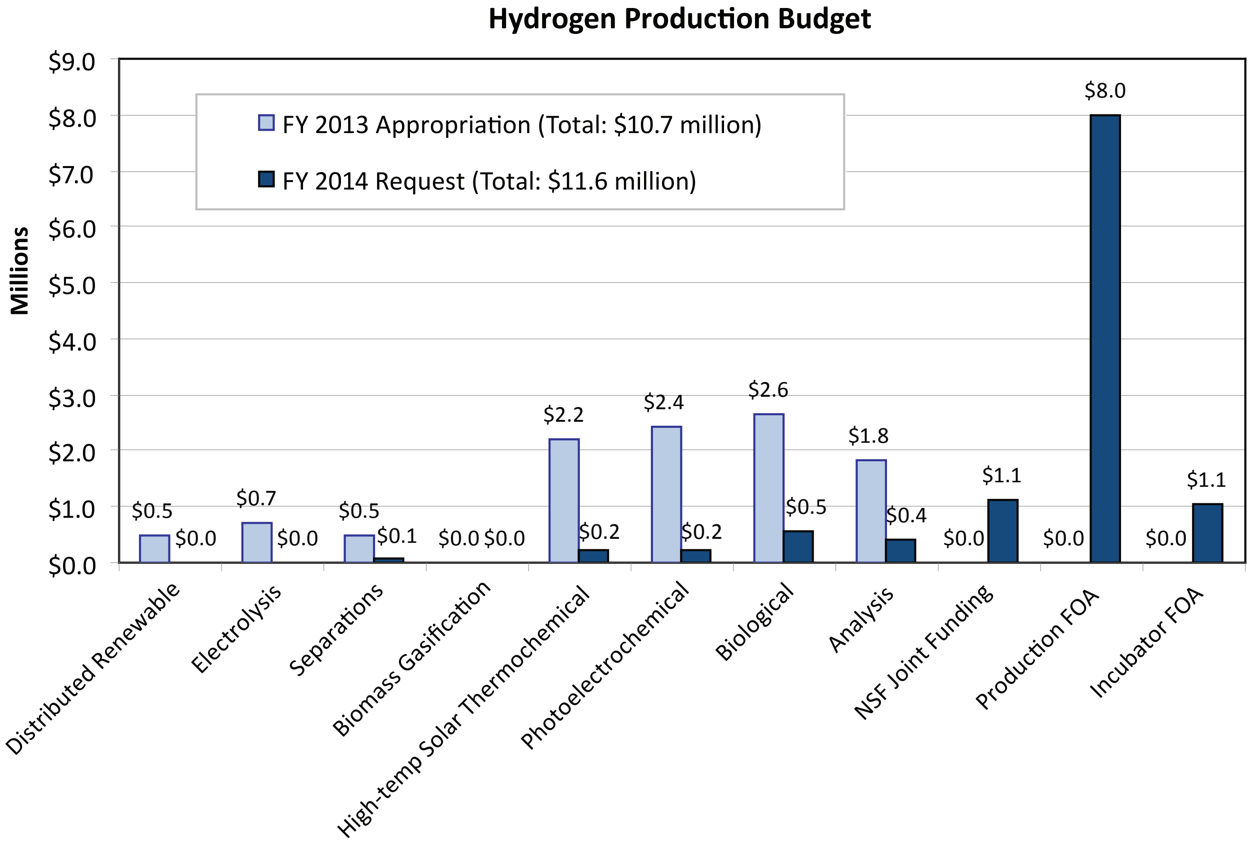
- Developed a comprehensive PEM Electrolysis H2Av3 Case Study based on input from four electrolyzer companies with PEM electrolysis expertise. (SAIC/NREL)

BUDGET

The FY 2013 appropriation for the Hydrogen Production and Delivery program of the FCTO was $15.7 million. Funding was distributed approximately 68% to 32% between Production and Delivery, respectively (approximately the same distribution used in FY 2012).

The request for Production and Delivery in FY 2014 is $21 million. The estimated budget breakdown for Production funding in FY 2014 is shown in Figure 2. Production has increasingly focused in past years on early development, long-term, renewable pathways such as photoelectrochemical, biological, and solar-thermochemical hydrogen production. This trend will likely continue in FY 2014 as new projects are selected from funding opportunities. However, innovative approaches to renewable or reduced carbon technologies for nearer-term distributed and/or semi-central production will also be considered for funding when appropriate.

[8] *Efficient Generation of H2 by Splitting Water with an Isothermal Redox Cycle*, Christopher L. Muhich et.al., Science 341, 540 (2013).



NSF – National Science Foundation; FOA – Funding Opportunity Announcement

FIGURE 2. HYDROGEN PRODUCTION BUDGET. Budget amounts for FY 2013 and projected amounts for FY 2014, contingent upon appropriations, are shown broken down by the different production pathways. Exact distribution of funds in FY 2014 will not be defined until funds have been appropriated and new projects selected.

FY 2014 PLANS

General Hydrogen Production program plans for FY 2014 include:

- Prepare and post a report on the Biological Hydrogen Production Workshop; and release a Request for Information inviting further input. Outcomes of the workshop and responses to the Request for Information will be used to inform programmatic planning.
- Continue to develop and update hydrogen production pathways analyses with the H2Av3 tool and develop a case study on fermentative hydrogen production and establishment of cost and performance baselines for new project starts.
- Continue emphasis on materials durability, production efficiency and process optimization for all pathways, and develop and refine materials characterization protocols and performance metrics for early development technologies.
- Continue coordination with the Office of Science, which funds basic research related to hydrogen and fuel cell technologies. Together with Basic Science activities, a fundamental understanding of issues related to hydrogen production (particularly in the longer-term R&D areas of photoelectrochemical and biological processes) can help address the challenges of hydrogen production. Coordination of the solar-hydrogen-related fundamental research activities in the Office of Science's Solar Fuels Innovation Hub with the EERE's hydrogen production systems-oriented R&D will be a high priority.
- Initiate RD&D projects in Production R&D through competitive funding opportunities, including a topic on renewable hydrogen for joint funding by the National Science Foundation and the FCTO.

- Validate and assess performance and design of composite separation membranes, as well as production methods to produce commercial quantities of substrates and membranes at reasonable cost. Perform economic analysis based on test results obtained to estimate costs for commercial equipment and membranes. (FE)

Important pathway-specific milestones planned for FY 2014 in the Hydrogen Production program projects include:

- Achieve continuous hydrogen photoproduction for at least 30 minutes (10x longer than wild type) with an average rate of at least 2.8 umol H_2 mg Chl-1 h^{-1}, by whole cells of a Ca1-expressing mutant strain of the alga *Chlamydomonas reinhardtii* under full solar-light intensities, in the presence of the uncoupler FCCP (mesoxalonitrile 4-trifluoromethoxyphenylhydrazone) measured continuously by the Clark electrode.
- Reduce electrolyzer cell precious metal cathode catalyst loading by 90%, compared to a baseline commercial membrane electrode assembly, to 0.12 mg/cm^2 while maintaining equivalent performance of at least 2.0 V at 1.75 A/cm^2.
- Apply nitrogen ion implantation surface passivation treatment to p-InP, a III-V semiconductor that could enable PEC water splitting efficiencies in excess of 20% solar-to-hydrogen, and evaluate the corrosion mitigation.
- Demonstrate a H_2 redox capacity of ≥300 µmole/g for one or more reaction cycles for particle-based STCH production, compared to the 2012 baseline for ceria of 150 µmole/g (at a reduction temperature of 1,550 C), indicating the potential to achieve the 2015 targets of 10% solar-to-hydrogen efficiency and 8.1E-07 kg/s m^2 production rate.

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