

II.1.2 Solar High-Temperature Water-Splitting Cycle with Quantum Boost

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Objectives

- Evaluate photo/thermo-chemical water splitting cycles that employ visible portion of the solar spectrum for production of hydrogen.
- Select a solar-unique cycle that has the best potential for cost-effective production of hydrogen from water and meeting the DOE target of \$3.00/gasoline gallon equivalent (gge) at the plant gate.
- Demonstrate technical feasibility of the selected cycle using solar input in bench-scale reactors.
- Demonstrate pre-commercial feasibility via a fully-integrated pilot-scale solar hydrogen production plant.
- Perform techno-economic analysis of the selected solar-unique cycle having a production capacity of 100 metric tons of hydrogen per day.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (October 2007 edition):

- (U) High-Temperature Thermochemical Technology
- (V) High-Temperature Robust Materials
- (W) Concentrated Solar Energy Capital Cost
- (X) Coupling Concentrated Solar Energy & Thermochemical Cycles

Contribution to Achievement of DOE Hydrogen Production Milestones

This project directly contributes to achievement of the following DOE milestone as outlined in the section 3.1.5 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan – Planned Program Activities for 2005-2015 (October 2007 edition), Hydrogen Production Task 6: High-Temperature, Solar-Driven, Thermochemical Processes.

- **Task 6 – Milestone 22:** Down-select to 5-10 promising high-temperature solar-driven thermochemical cycles for R&D based on analysis and initial laboratory work.

Technical Targets

Table 1 presents the progress made, to date, in achieving the DOE technical targets as outlined in the section 3.1.4 Multi-Year Research, Development and Demonstration Plan – Planned Program Activities for 2005-2015 (October 2007 edition), Table 3.1.9: Solar-Driven, Thermochemical High-Temperature Thermochemical Hydrogen Production.

Accomplishments

- Completed review and analysis of potential solar thermochemical water splitting cycles.
- Selected the sulfur-ammonia (SA) cycle, with ZnO sub-cycle, for further development.
- Experimentally validated the photocatalytic hydrogen production step increasing the efficiency of the photocatalyst to 28.2% (defined as the lower heating value [LHV] of H₂ generated divided by the high radiant energy streaming into the photoreactor with wavelengths in the range of $\lambda = 300\text{-}520$ nm).

TABLE 1. Progress Towards Meeting Technical Targets for Solar-Driven High-Temperature Thermochemical Hydrogen Production

Characteristics	Units	DOE 2008 Target	Project Status
Solar-Driven High-Temperature TCWSC Hydrogen Production Cost	\$/gge H ₂	10.00	\$2.25-\$4.12/kg ^a
Heliostat Capital Cost (installed cost)	\$/m ²	180	105
Process Energy Efficiency ^c	%	25	51 ^b

^a Preliminary, H2A analysis to be completed.

^b The process energy efficiency is defined as the energy of the hydrogen produced (LHV) divided by the sum of the energy from the solar concentrator system plus any other net energy required for the process. An implicit assumption made in the construction of the AspenTM flowsheet from which this efficiency figure was obtained is that the output from the photocatalytic reactor is in sufficient quantity to meet the requirements of the low- and high-temperature thermocatalytic reactors, i.e. the SA plant operates as a closed-cycle.

TCWSC - thermochemical water splitting cycle

- Validated the oxygen production sub-cycle demonstrating that ammonia can be recovered completely and separately during the lower temperature thermocatalytic reaction with no contamination by sulfur dioxide and/or oxygen.
- Demonstrated that the high temperature oxygen evolution reaction can be completed quantitatively and efficiently at less than 850°C temperature.
- Performed preliminary evaluation of solar collector configurations and reactor/receiver options for the cycle.
- Completed the AspenTM flowsheeting of the SA cycle and performed a detailed analysis of all thermochemical and unit operation processes with full chemical recycle.
- Closed and optimized the AspenTM flow sheet of the SA cycle; estimated the maximum 1st Law thermodynamic efficiency of the cycle (defined as the ratio of the LHV of the hydrogen generated divided by the solar energy input to the cycle) to be about 51%.
- Estimated preliminary hydrogen production costs of \$2.25/kg to \$4.12/kg – depending on the configuration of the solar concentrator array and design of the photoreactor.
- Identified an option for potential heliostat cost savings using glass-reinforced concrete (GRC) as a structural material.



Introduction

A limitation of most solar thermochemical cycles proposed for water splitting is that they do not take

advantage of the unique characteristics of the solar resource. For example, the spectrum of sun light contains ultraviolet and visible radiation that are very energetic and able to trigger photocatalytic reactions. Many solar thermochemical cycles ignore the potential of these photons and use their energy only as heat to drive thermochemical reactions. In the SA cycle, the photonic energy of solar spectrum is used directly to fuel the hydrogen evolution step of the cycle. This means that less thermodynamic “work” is needed in the other steps of the cycle, so the high-temperature oxygen production reactors can operate cooler and thus be smaller and less expensive. Furthermore, the lower temperatures reduce the requirements on the solar concentrator field and its associated costs. This can lead to a process that fully utilizes the solar spectrum and produces hydrogen at lower cost than other thermochemical processes.

The benefit from developing and implementing this process will be more cost-effective production of hydrogen from clean solar energy with no effluents or waste products. The process has potential for accelerating the implementation of the hydrogen economy by producing hydrogen cleanly and at the DOE cost target.

Approach

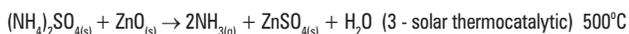
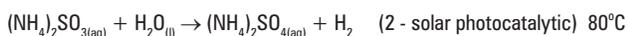
The approach used in this project is to evaluate options for unique solar water splitting cycles and select a preferred process based on chemical feasibility, potential for high efficiency, and lower costs. More specifically, we are to perform laboratory testing of all process steps within the prospective cycle in order to improve yield, verify the chemistry, and validate the overall cycle performance. Once all process steps have been validated and well understood at laboratory scale, the expectation is to integrate the thermochemical plant with an appropriate solar collector field for pilot scale testing with sunlight. Finally, in parallel with the chemical and solar testing, we continually re-assess the economics of the process to verify its cost-effectiveness compared to other hydrogen production processes.

Results

Cycle Evaluation and Analysis

We have evaluated many potential thermochemical cycles that might involve a photocatalytic step for hydrogen and/or oxygen production. Cycles were reviewed based on technical feasibility, potential for high solar-to-hydrogen conversion efficiency, and prospects of the cycle to be implemented cost-effectively. The analysis included seven “actively pursued” cycles. The SA cycle was selected as the most promising candidate.

The SA cycle is depicted in Figure 1 and the reactions involved are given below:



In this cycle, ammonium sulfite is photocatalytically oxidized to ammonium sulfate, releasing hydrogen gas from the aqueous solution. The ammonium sulfate reacts in a low-temperature reactor with zinc oxide forming ammonia and zinc sulfate. Zinc sulfate flows to a higher temperature reactor where it is decomposed into sulfur dioxide, water vapor, and oxygen gas. Finally, the ammonia and sulfur dioxide are reacted in the presence of water to re-generate the ammonium sulfite solution and close the cycle. All the intermediate chemicals are recycled, so the net reaction is water splitting to form hydrogen and oxygen gas.

The SA cycle has many advantages, including easy separations of the products. The photocatalytic hydrogen production step (2) occurs at near ambient temperatures under one sun. The oxygen is evolved in step (4), and can be easily separated from the SO_2 and water vapor. Reactions (2) and (3) utilize ZnO and ZnSO_4 within which ZnO is reacted to form zinc sulfate in the low-temperature reactor and regenerated from ZnSO_4 in the high temperature reactor – with the net effect being decomposition of ammonium sulfate to ammonia, sulfur dioxide and oxygen. The ZnO and ZnSO_4 are easily handled as solids and zinc oxide

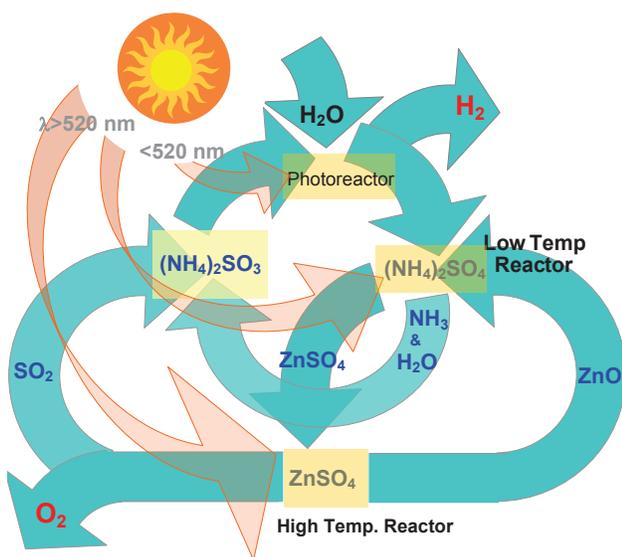


FIGURE 1. FSEC SA Solar Thermochemical Water Splitting Cycle

actually catalyzes the zinc sulfate decomposition step so it can be performed at lower temperatures.

Laboratory Testing of H_2 Evolving Step and ZnO - ZnSO_4 Sub-Cycle

Experiments have been performed on both the hydrogen and oxygen production reactions of the SA cycle. Photocatalyst screening has been conducted with single and multiple-component catalysts to increase the efficiency of the hydrogen production photo-process. The most efficient photocatalyst found to date consisted of electronic-grade cadmium sulfide doped with small amounts of Pt, Pd, and Ru. This photocatalyst generated hydrogen with an energy conversion efficiency of about 28.2%.¹ Figure 2 depicts the effect of photocatalyst doping on the efficiency of the hydrogen production process. Other tests have confirmed the long-term stability of the photo-system (over many days), the effects of temperature on the photocatalytic reactions, and the enhancement effects of polymer stabilization of the colloidal particles in the photolyte. Figure 3 shows the long-term performance of the photocatalyst.

The oxygen evolution subcycle has been investigated using thermogravimetric/differential thermal analysis-mass spectrometry, temperature programmed desorption-mass spectrometry, ion chromatography, gas chromatograph mass spectrometry, and ultraviolet-visual spectrometric methods. Tests have shown that the chemistry of the ammonium sulfate/zinc oxide reaction has fast reaction kinetics and generates ammonia, H_2O and zinc sulfate, with no undesirable byproducts, and

¹ Defined as the energy contained in the hydrogen produced (LHV) per unit time divided by the light flux from AM1.5 solar simulator at wavelengths in the range of 300-520 nm illuminating the photolyte.

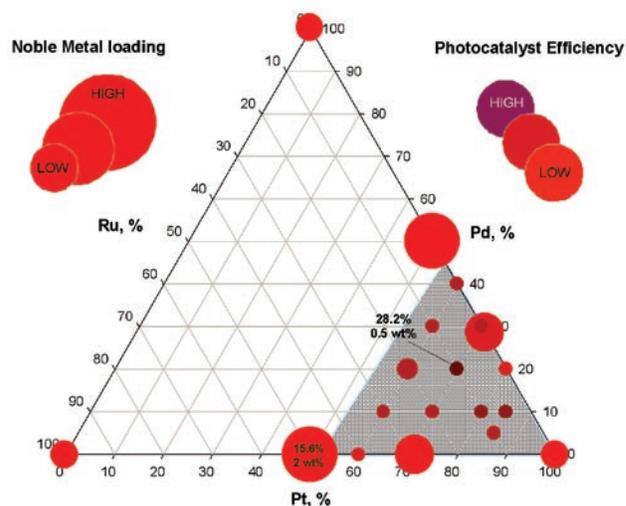


FIGURE 2. Effect of Noble Metal Doping on the Hydrogen Production Efficiency of CdS Photocatalyst

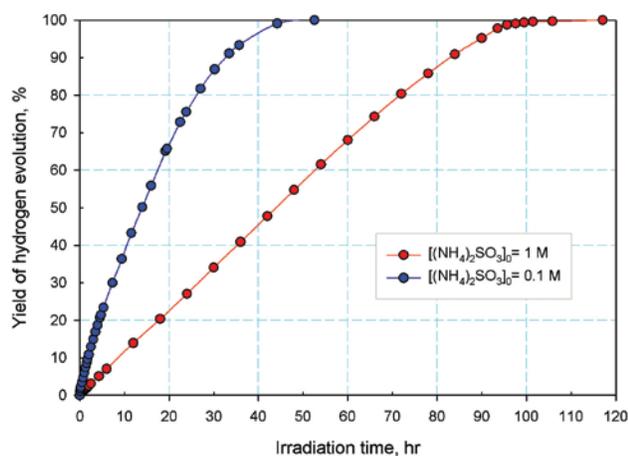


FIGURE 3. Effect of initial sulfite concentration, $[(\text{NH}_4)_2\text{SO}_3]_0$, on the rate of H_2 evolution during extended runs – photolyte volume: 300 mL, photocatalyst (noble metal doped CdS) loading: 1.67 mg/mL of photolyte, noble metal (70 wt% Pt; 20 wt% Pd; 10 wt% Ru) loading: 0.5 wt% of CdS (500 mg).

that the evolution of ammonia and water vapor occurs below about 500°C, while evolution of sulfur oxides and oxygen is observed only above about 700°C. These results confirmed the facile chemistry and simplicity of the high temperature oxygen production steps of the SA cycle.

Solar Concentrator Configuration and Analysis

SAIC has performed preliminary analysis of the characteristics and requirements of the solar collector field for the SA cycle. There are competing requirements for the solar collector field:

- Due to the high temperatures involved in the oxygen evolution step, only concentrating systems are feasible for conducting those reactions. The difficulties of transporting, distributing, and processing solid materials in a field of dishes, and the scale of a large central hydrogen plant makes a heliostat/central receiver the most feasible option.
- The hydrogen evolution process involves one-sun illumination of the photoreactor near ambient temperature. This would be best accomplished with a flat-plate collector configuration that is also a photoreactor – fabricated using polymeric materials.
- The concept originally proposed used a beam-splitting approach to separate the high-energy photons utilized in the photoreactor from infrared radiation used in the thermocatalytic reactions. This concept increases the solar energy-to-hydrogen conversion efficiency of the process by allowing the ultraviolet and infrared portions of the spectrum to be used efficiently. So, consideration has been given to the implementation of a hot- or cold-mirror

system for splitting the solar spectrum directed to the reactors.

Several collector configurations were proposed and evaluated, involving dishes, heliostats, and hot and cold mirrors. The configurations were as follows:

- Dish concentrator with hot mirror reflector, thermal receiver at the focus, and photoreactors flat behind the parabolic dish.
- Dish concentrator with full spectrum mirrors and a thermal receiver at the focus, but with a cold mirror reflector near the dish focus and a cylindrical photoreactor concentric to the dish axis and outside the diameter of the dish.
- Conical concentrator with hot-mirror reflector, a line-focus thermal receiver along its axis, and a photoreactor flat behind the conical reflector.
- Heliostat field with hot mirror reflectors and a thermal receiver on the tower, with photoreactors on the heliostat behind the hot mirrors, or on the ground beneath the heliostats.
- Heliostat field with full-spectrum mirrors focused on a thermal receiver on the tower, with a separate field of flat-plate photoreactors.

Preliminary evaluation of these configurations led to elimination of all the dish concepts for full-scale systems due to material handling difficulties and lack of scalability. The separate central receiver/reactor system provides some flexibility that could reduce the cost of hydrogen produced at the expense of solar energy conversion efficiency. The evaluation is continuing.

Heliostat Cost Reduction

One clear conclusion that came out of the collector evaluation was that the heliostats in a central receiver system are a (or even “the”) major cost component of the system. SAIC identified a potential for cost savings in heliostat fabrication using glass-reinforced concrete to replace the steel structure of the heliostats. Several design concepts were drawn together to produce a design with reduced system cost, as follows:

- Extremely low cost structural material (approximately \$0.15/kg).
- Spray-up fabrication process on low-cost mold, with molded-in features such as ribs and mounting provisions.
- Small size (10-15 m²) to facilitate fabrication, transport, handling, installation, and maintenance.
- Reduced wind loading due to ground-hugging design; sufficient mass in structure to limit foundation requirement for lift loads.
- Factory assembled unit to reduce field installation labor.

- Factory-produced, surface-installed concrete track foundation to minimize site preparation and installation costs, while maintaining good accuracy.
- Low-cost, low-power drive system.
- Self-powered heliostat using photovoltaic panel for direct current power to eliminate field power wiring.
- Wireless communication to eliminate field control wiring.

The result of all these innovations is a heliostat with a projected production cost well below \$100/m², compared to conventional heliostats at about \$129/m² for high volume production [1]. Figure 4 presents a computer model of a potential prototype unit.

Economic Analysis

A comparison was made between the SA cycle and the hybrid sulfur (HyS) process that has been studied by Sandia National Laboratories [2]. In the Sandia analysis, a large central hydrogen production plant was designed, costs were estimated for the components of the solar and chemical plant, and the cost of hydrogen from the plant was projected.

To compare with the HyS process, adjustments were made to the plant configuration as follows:

- Estimated SA process efficiency vs. HyS process efficiency.
- Estimated solar field efficiency for 850°C receiver vs. 1,100°C receiver.
- Estimated cost of plastic film solar photoreactors.
- Estimated present costs and performance characteristics of hot and cold mirrors.
- Estimated costs of GRC and conventional heliostats.

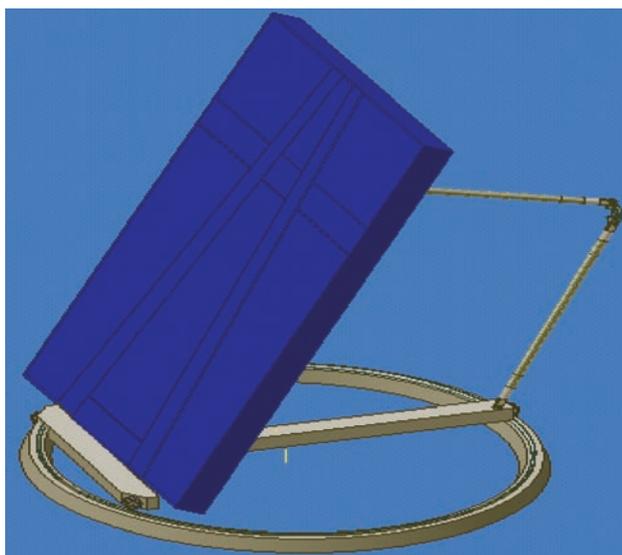


FIGURE 4. SAIC Glass-Reinforced Concrete Heliostat Design

The results of this preliminary evaluation are summarized in the following table:

	Area of Solar Reflectors (sq. km)	Total Land area (sq. km)	Total Capital Cost (\$M)	Projected Cost of H ₂ (\$/kg)
Baseline hybrid sulfur heliostat (Kolb)	1.30	6.50	381.2	3.00
SA heliostat with hot mirror	1.06	5.31	810.6	4.12
SA heliostat-separate photoreactor	0.84	5.90	435.1	2.33
SA advanced heliostat-separate photoreactor	0.84	5.90	417.4	2.25

The SA process shows the potential to reduce the size of the heliostat field from 1.3 sq km to 0.84 sq km, and to reduce the land area (even with a separate photoreactor system) from 6.5 sq km to 5.9 sq km or less. The improvements are mainly due to the high efficiency of the FSEC process and the reduction in the temperature of the hot reactor, leading to higher solar receiver efficiency. The hot-mirror system showed slightly worse economics than the baseline system, mainly due to the estimated cost of the hot mirrors, but the systems with separate photoreactors showed significant reductions in the cost of hydrogen produced. Use of an advanced (GRC) heliostat produced even larger savings. These results are encouraging regarding the potential for the SA cycle to deliver hydrogen cost-effectively.

Conclusions and Future Directions

In the first few months of this project, we completed an evaluation of thermochemical cycles and concluded that the sulfur-ammonia cycle developed by FSEC has excellent potential. The chemistry of the process has been validated in laboratory conditions, including demonstration and improvement of the photocatalytic H₂ production process and validation of the oxygen evolving thermocatalytic decomposition of zinc sulfate. Preliminary evaluation has led to selection of a heliostat field with a secondary concentrator and a cavity receiver as the collector field configuration.

Activities planned for the upcoming year (assuming continued funding) include:

- Completion of SA cycle testing and optimization, including determination of reaction kinetics needed for proper sizing of the chemical reactors.
- Fabrication and testing of a sub-scale heliostat with a GRC structure.

- Refinement of the economic analysis and generation of a preliminary H₂A economic model of a full-scale hydrogen production plant.
- Preliminary design of the photocatalytic and thermocatalytic reactors and materials handling equipment for the pilot-scale plant, in preparation for the full-scale plant design.

The results of these tasks should further validate this cycle as one that produces hydrogen from solar energy via water splitting at a competitive cost. The next phase of the project will demonstrate on-sun production of hydrogen in a flat plate reactor/receiver – in preparation for fabrication and testing of the pilot-scale hydrogen production system in Phase III.

Special Recognitions & Awards/Patents Issued

1. Huang, C., Tabatabaie-Raissi, A., Muradov, N.Z. “A Thermochemical Cycle for Production of Hydrogen and/or Oxygen via Water Splitting Processes,” Pub. No.: WO/2007/002614 International Application No.: PCT/US2006/024865.
2. Huang, C., Tabatabaie-Raissi, A., Muradov, N.Z. “Solar Metal Sulfate – Ammonia Based Thermochemical Water Splitting Cycles for Hydrogen Production,” US Provisional Patent, Serial No. 60/986,820, Nov., 2007.

FY 2008 Publications/Presentations

1. Taylor, R., Davenport, R., T-Raissi, A. “High Efficiency Solar Production of Hydrogen from Water,” *NHA Annual Hydrogen Conference*, April 2008.
2. Davenport, R., Taylor, R., and T-Raissi, A., “Solar Concentrator Options for a Thermochemical Hydrogen Production Process,” presentation at the *ASES SOLAR2008 Conference*, San Diego, CA, 4-8 May 2008.
3. Huang, C., T-Raissi, A., Fenton, S., Mao, L., and Muradov, N., “A New Family of Solar Metal Sulfate–Ammonia Based Thermochemical Water Splitting Cycles for H₂ Production,” presentation at the *ASES SOLAR2008 Conference*, San Diego, CA, 4-8 May 2008.
4. T-Raissi, A., Huang, C., Muradov, N.Z., Mao, L., Fenton, S., Yao, W., Block, D.L., Illiassou, B., Taylor, R., and Davenport, R., “Solar-Driven Photocatalytically-Assisted Water Splitting,” presentation at the *DOE Hydrogen Program Review Meeting*, 10 June 2008, Crystal City, VA.
5. Taylor, R. and Davenport, R., “Solar Field Configuration for Thermochemical Hydrogen Production with Quantum Boost,” presentation at the *WHEC2008 Conference*, Brisbane, Queensland, Australia, 15-19 June 2008.

6. Taylor, R., Davenport, R., and T-Raissi, A., “Prospects for the Solar Thermochemical Production of Hydrogen from Water,” poster presented at the *WHEC2008 Conference*, Brisbane, Queensland, Australia, 15-19 June 2008.
7. Fenton, S., Huang, C., Muradov, N., and T-Raissi, A., “Flowsheeting a Solar-Driven Sulfur-Ammonia Water Splitting Cycle with ZnSO₄-ZnO Sub-Cycle,” poster presentation at the *WHEC2008 Conference*, Brisbane, Queensland, Australia, 15-19 June 2008.
8. Mao, L., Huang, C., Yao, W., T-Raissi, A., and Muradov, N., “Development of High Efficiency Photocatalysts for Solar Hydrogen Production,” presentation at the *WHEC2008 Conference*, Brisbane, Queensland, Australia, 15-19 June 2008.
9. Mao, L., Huang, C., T-Raissi, A., and Muradov, N., “Zinc Oxide Mediated Thermal Decomposition of Ammonium Sulfate,” presentation at the *WHEC2008 Conference*, Brisbane, Queensland, Australia, 15-19 June 2008.
10. Huang, C., Illiassou, B., Mao, L., T-Raissi, A., Muradov, Z. “Development of Efficient Photocatalysts for Solar Hydrogen Production,” *Proc. of 17th World Hydrogen Energy Conference*, 15-19 June 2008, Brisbane, Australia.
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14. T-Raissi, A., Huang, C., Muradov, N. “A New Solar Thermochemical Water Splitting Cycle for Hydrogen Production,” *Proc. Int. Symp. on Materials Issues in A Hydrogen Economy*, Richmond, Virginia, Nov., 2007.
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1. Kolb, G. et al., 2007. “Heliostat Cost Reduction Study,” SAND-2007-3293, Sandia National Labs.
2. Kolb, G., Diver, R., and Siegel, N., 2005. “Central-Station Solar Hydrogen Power Plant,” proceedings of ISEC 2005, ASME Int. Solar Energy Conference, Orlando, FL, 6-12 August.