II.F.2 Solar High-Temperature Water-Splitting Cycle with Quantum Boost

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Subcontractors:

- University of Central Florida, Florida Solar Energy Center (FSEC), Cocoa, FL
- Electrosynthesis Co. (ESC), Inc., Lancaster, NY

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Project End Date: August 31, 2014

Objectives

- Demonstrate a cost-effective high-temperature water splitting cycle for hydrogen production using concentrated solar energy.
- Evaluate photocatalytic and electrolytic options for generating hydrogen that meet DOE's solar high temperature H_2 production efficiency and cost goals
- Confirm the feasibility of the selected cycle via bench-scale experiments.
- Determine the economic prospects of the selected cycle using the Aspen Plus™ chemical process model and H2A economic analysis program.
- Demonstrate a fully-integrated pilot-scale solar H_2 production unit.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

Table 1 presents the progress made, to date, in achieving the DOE technical targets as outlined in the §3.1.4 Multi-Year Research, Development and Demonstration Plan – Planned Program Activities for 2005-2017 (updated Oct. 2007 version), Table 3.1.9: Solar-Driven, Thermo-chemical High-Temperature Thermochemical Hydrogen Production.

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

Characteristics	Units	U.S. DOE Targets			Project Status
		2008	2012	2017	
Solar-Driven High-Temperature TCWSC Hydrogen Production Cost	\$/gge H_2	10.00	6.00	3.00	\$5.98/ \$5.05 [a]
Heliostat Capital Cost (installed cost)	\$/m^2	180	140	80	97[b]
Process Energy Efficiency[c]	%	25	30	>35	19.3

[a] Electrolytic/photocatalytic system projected costs based on revised H2A analysis.
[b] Based on SAIC glass-reinforced concrete structure with 10 sq.m. area and low production quantity.
[c] Plant energy efficiency is defined as the energy of the hydrogen produced (lower heating value) divided by the sum of the energy delivered by the solar concentrator system plus any other net energy imports (electricity or heat) required for the process.
[d] Electrolytic sulfur-ammonia (SA) thermochemical water-splitting cycle efficiency based on the most recent Aspen+ flow sheet analysis.
gge – gasoline gallon equivalent; TCWSC – thermochemical water splitting cycle

Accomplishments

- Quantitative hydrogen production using an electrolytic cell with efficient sulfite oxidation was verified.
- The voltage of the electrolytic cell was reduced from 1.2 V to less than 1.0 V by increasing temperature/pressure, controlling pH and improving cell design.
- A short-term electrolytic cell test achieved 0.63 V at 186 mA/sq.cm using a proprietary new design/catalyst.

- The basic feasibility of the all-(liquid/gas) $K_2SO_4/K_2S_2O_7$ chemistry for the high-temperature oxygen evolution sub-cycle using potassium sulfate has been demonstrated, but more lab testing is needed.
- A mass balance on the oxygen evolution half cycle was performed using three sources of data; theoretical, thermogravimetric analysis (TGA) measurements and reactor experiments.
- A preliminary economic analysis based on the previously fabricated half-scale prototype glass-reinforced concrete (GRC) heliostat indicates that the cost can be reduced from $126/m^2 to $90/m^2.
- Using the Aspen Plus^{TM} Process Design and Analysis model, trade-off studies were performed to optimize the overall plant configuration, e.g.:
  - Electrical heating of the sulfur trioxide reactor was shown to be not cost-effective compared to direct solar heating.
  - Electrical production from steam and ammonia in the process was shown to be sufficient to power the electrolytic process.
  - Drying the aqueous ammonium sulfate material to solid form was shown to have little or no advantage over using it in aqueas form.
- Using the H2A economic model, the hydrogen production costs were determined to be $5.98/kg for the electrolytic SA cycle with $K_2SO_4/K_2S_2O_7$ sub-cycle.

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Introduction

The source of hydrogen must be sustainable and the process to produce hydrogen must be efficient and thus cost-effective compared to conventional energy. The thermo-chemical production of hydrogen by splitting water with solar energy is a sustainable and renewable method of producing hydrogen. The process must be proven to be efficient and cost-effective. 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. The spectrum of sun light contains ultraviolet and visible photons that are very energetic and able to trigger photocatalytic reactions. In the photocatalytic SA cycle, the photonic portion of the solar spectrum is used directly to accomplish the hydrogen evolution step of the cycle. This means that less energy is needed in the high-temperature oxygen production part of the cycle.

Many thermochemical water splitting cycles studied to date have difficult and/or costly product separation steps and materials handling and safety challenges. An example of the former is the Zn/ZnO cycle that requires rapid quenching of the high-temperature Zn-O_2 mixture to prevent unwanted back-reaction to ZnO. An example of the latter is the Cd/CdO cycle that involves handling and processing of toxic cadmium metal at high temperatures. On the other hand, the sulfur-ammonia cycle has potential to circumvent these and other shortcomings of the legacy thermochemical water splitting cycles while meeting the DOE hydrogen production cost targets.

Approach

To achieve the project objectives, the Bowman-Westinghouse "sulfur-family", hybrid thermochemical water splitting cycle ("Hybrid Sulfur, HyS" cycle) was selected and modified by introducing ammonia as the working reagent (thus sulfur-ammonia, or "SA," cycle) to attain a more efficient solar interface and less problematic chemical separation steps. Several versions of the SA cycle were developed and evaluated experimentally, as well as analytically using the Aspen Plus^{TM} chemical process simulator.

Two approaches were considered for the hydrogen production step of the SA cycle, namely: photocatalytic and electrolytic oxidation of ammonium sulfite to ammonium sulfate in an aqueous solution. Also, two sub-cycles have been considered for the oxygen evolution side of the SA cycle, namely: zinc sulfate/zinc oxide and potassium sulfate/potassium pyrosulfate sub-cycles. The laboratory testing and optimization of all the process steps for each version of the SA cycle were then carried out. Once the optimum configuration of the SA cycle has been identified and the cycle has been validated in closed-loop operation in the lab, it will be scaled up and tested on-sun.

Results

Cycle Evaluation and Analysis

In previous years, significant work was performed on the photo-catalytic SA cycle. During the past year, efforts have been redirected to the electrolytic SA cycle. The electrolytic SA cycle is summarized in the following equations:

1. $SO_{2(g)} + 2NH_{3(g)} + H_2O_{(l)} \rightarrow (NH_4)_2SO_{3(aq)}$ (1 – chem. absorption) 25°C
2. $(NH_4)_2SO_{3(aq)} + H_2O_{(l)} \rightarrow (NH_4)_2SO_{4(aq)} + H_2$ (2 – electrolytic) 80°C
3. $(NH_4)_2SO_{4(aq)} + K_2SO_{4(l)} \rightarrow K_2S_2O_{7(l)} + 2NH_{3(g)} + H_2O_{(g)}$ (5 – solar thermal) 400°C
4. $K_2S_2O_{7(l)} \rightarrow K_2SO_{4(l)} + SO_{3(g)}$ (6 – solar thermal) 550°C
5. $SO_{3(g)} \rightarrow SO_{2(g)} + \frac{1}{2} O_{2(g)}$ (7 – solar thermal) 850°C

The electrolytic oxidation of the ammonium sulfite solution occurs above ambient temperature at reasonably low pressures. Reactions (3) and (4) form a sub-cycle by which potassium sulfate is reacted with ammonium sulfate in the low-temperature reactor, to form potassium thiocyanate. That is then fed to the medium-temperature reactor where it is decomposed to SO_3 and K_2SO_4 again, closing the sub-cycle. The potassium sulfate and thiocyanate form a miscible liquid melt that facilitates the separations and the movement of the chemicals in reactions (3) and (4). The oxygen production step (5) occurs at high temperature over a catalyst. Separation of the oxygen from SO_2 occurs when they are mixed with water in reaction (1). The net cycle reaction represented by reactions 1-5 is decomposition of water to form hydrogen and oxygen. All of the reaction steps described above have been demonstrated in the laboratory and shown to occur without undesirable side reactions. Figure 1 depicts the high-temperature reactions in a pictorial fashion.

Electro-Oxidation of Aqueous Ammonium Sulfite Solutions

Optimization of the electrolytic process continued at both ESC and FSEC. FSEC developed a proprietary catalyst and briefly demonstrated a divided cell at 0.63 V and 186 mA/cm^2. In a further development, an electrolytic cell with no Nafion® separator was also run. ESC tested operation of cells at elevated temperature and showed that the voltage could be reduced below 1.0 V in a conventional electrolytic cell by operating at elevated pressure and temperature. Figure 2 shows results of electrolysis runs at elevated temperatures.

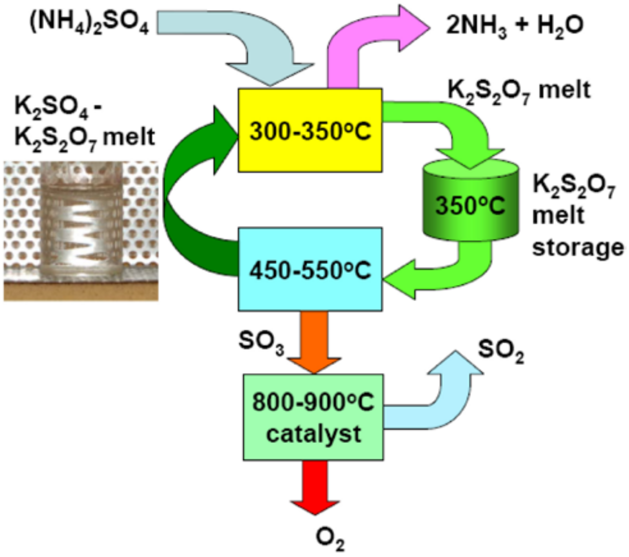

FIGURE 1. Pictorial Representation of High-Temperature Cycle Steps for the SA Water-Splitting Cycle

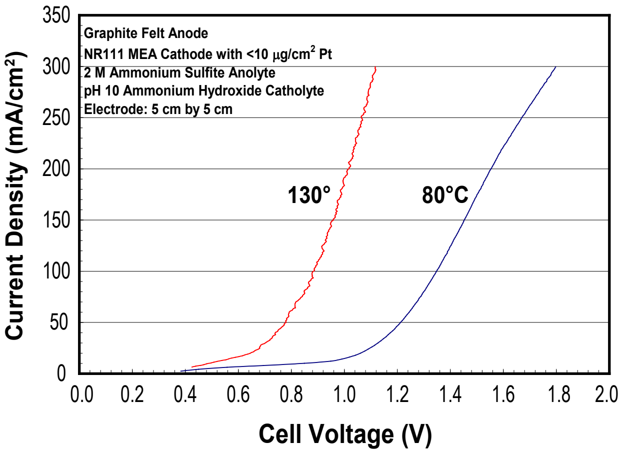

FIGURE 2. Electrochemical Test Results at Elevated Temperatures

High-Temperature Cycle Step Evaluation

Evaluation of the all-liquid/gas high-temperature cycle steps continued. As shown in Figure 3, TGA experiments were conducted to show the evolution of ammonia and water vapor, followed by evolution of sulfur trioxide at a higher temperature. A potential difficulty is the small temperature differences between these evolutions, which may make separation of the products more difficult. A mass balance was also successfully conducted to check that the experimental results matched the analytical predictions, as shown in Figure 4.

Solar Field Optimization

The solar field configuration continued to be updated as the thermochemical system evolved. The primary present activity is to incorporate the all-liquid $K_2SO_4/K_2S_2O_7$ system. A two-receiver heliostat field design has been created to separate the low-temperature and high-temperature receivers. For the highest temperature oxygen evolution process, consideration is being given to using dish concentrators in addition to the heliostat field for the other thermal processes. Control optimization to best use the variable solar resource was also performed.

Heliostat Cost Reduction

The half-scale prototype glass-reinforced concrete heliostat was successfully tested and evaluated, and design features to be carried over to a full-scale unit were identified. The cost of heliostats in low production was updated, with the results shown in Table 2. The estimated production cost is less than \$100/m^2, a reduction of over 25% from present-day heliostat costs.

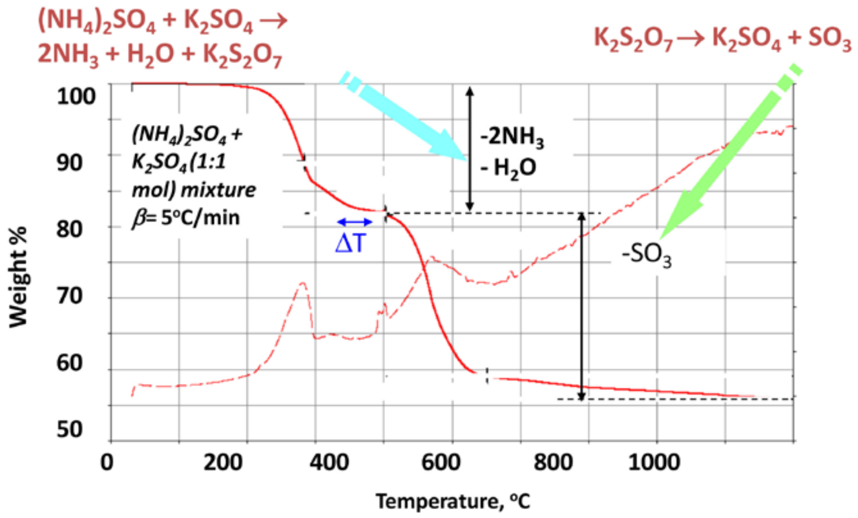

FIGURE 3. TGA Experimental Results for High-Temperature Subcycle

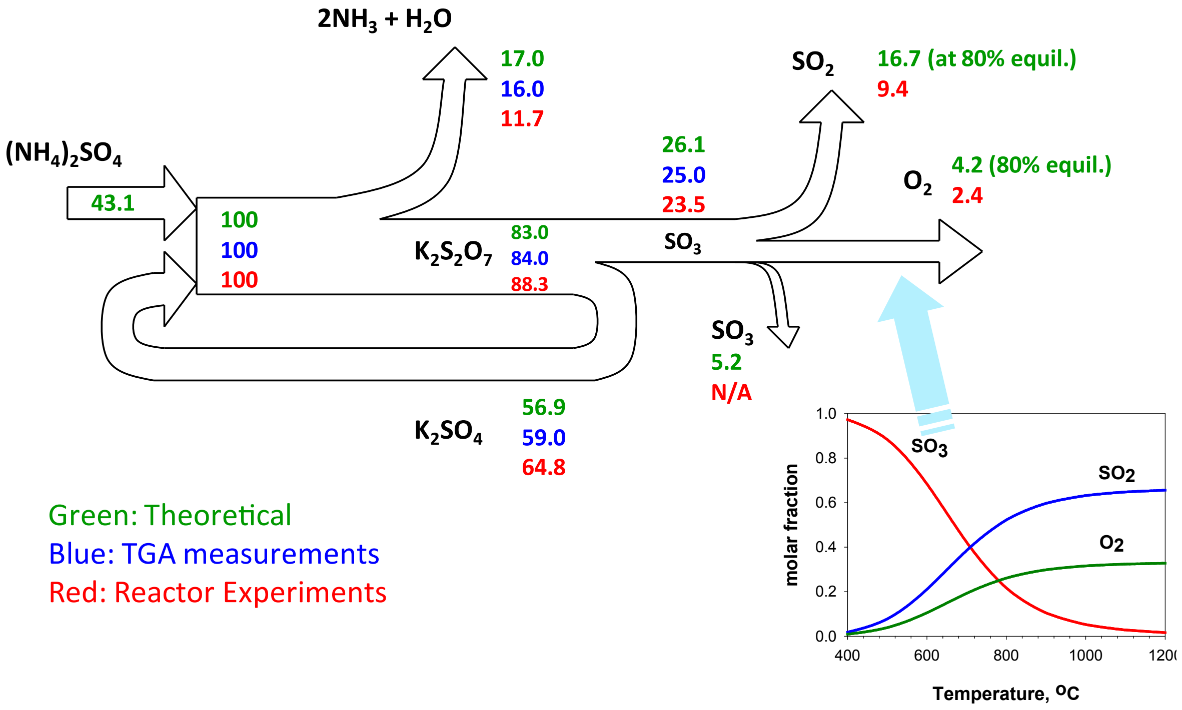

FIGURE 4. Mass Balance for the Oxygen Evolution Half-Cycle

TABLE 2. Cost of Low Production Heliostat

System Component	Cost per Square Meter
Concrete Structures	$ 13.31
Mirrors	$ 16.64
Control Electronics	$ 20.28
Drive components	$ 41.52
Other components	$ 5.00
Total	**$ 96.75**

Economic Analysis

The H2A economic model for the photocatalytic SA process with separate heliostat and photoreactor fields was updated. The resulting cost for hydrogen was found to be $5.05/kg, but the system solar efficiency was only 5.2% due to the large land area needed. The cost analysis of the electrolytic SA cycle was completed, with a resulting cost of $5.98/kg and an overall system efficiency of 19.3%. The H2A results are summarized in Table 3.

TABLE 3. H2A Results

Cost Component	Electrolytic System with Aqueous Am. Sulfate		Photocatalytic System with Separate Thermal and Photocatalytic Fields	
	Cost ($M)	% of Total	Cost ($M)	% of Total
Heliostat Field, Tower, & Receiver	$686	71.4%	$686	69.5%
Land	$11	1.1%	$11	1.1%
Electrolyzer/ Photocatalytic Reactor	$130	13.5%	$158	16%
Chemicals	$20	2.1%	$20	2%
Process Equipment	$113	11.8%	$113	11.5%
Total Capital Cost	**$960**	**100%**	**$988**	**100%**
Costs in $ per kg of hydrogen:	Cost:		Cost:	
Capital Cost	$5.39		$5.54	
Fixed Operation and Maintenance	$.92		$1.06	
Byproduct Credits	-$0.34		-$1.56	
Other Variable Costs, incl. Utilities	$0.01		$0.01	
Total Cost per kg of Hydrogen	**$5.98**		**$5.05**	

The H2A cost analysis program was also used along with Aspen Plus™ calculations to perform trade-off analyses on different configurations and process designs. In particular, the following trade-off analyses were performed:

- Using solar thermal vs. electricity to heat the reactor for the 900°C reaction to reduce SO_3 to SO_2 and O_2. It was determined that the solar thermal heat would provide higher efficiency.
- Reducing the aqueous ammonium sulfate to solid form before feeding to the low-temperature reactors. Drying the ammonium sulfate led to a lower system capital cost, but required more purchase of electricity from the grid. The cost of hydrogen was practically the same for both approaches ($6.21 vs. $5.98).

Conclusions and Future Directions

In summary:

- Significant progress was made in reducing the cell voltage and increasing the current density of the electrolytic cell.
- Initial evaluation of the all-liquid/gas high-temperature oxygen generation cycle steps appears to prove the subcycle feasibility.
- GRC continues to show promise to reduce heliostat cost substantially.
- Based on the work performed to date, it appears that the electrolytic SA cycle has the potential to meet DOE's near- and long-term H_2 production cost and efficiency goals.

Activities planned for the upcoming year include:

- Perform a thermodynamic analysis of the overall SA cycle to recheck earlier results, provide data to verify the cycle performance and ascertain if previous work by others may preclude the need to perform certain tasks. The complete SA cycle will be modeled using Aspen Plus™ to verify that the cycle can be closed and provide data to document the chemical plant analysis.
- Completion of optimization of the electrolytic process and cell. This will include identification of catalysts that will reduce the over-potential at the anode and allow operation at high current densities, and determining approaches to recombine anolyte and catholyte streams to control and maintain fixed pH.
- Complete evaluation of the K_2SO_4 oxygen subcycle reactions, including reaction kinetics.
- Finalization of the thermal reactor/receiver designs including materials specification and testing
- Finalization of the solar field configuration and design to match the final chemical plant requirements.
- Continue to update H2A economic analyses to document the potential cost of hydrogen from the SA cycle.

After completion of phase 1, the next phase of the project will involve laboratory validation of the closed-loop SA cycle leading to on-sun hydrogen production demonstration.

Special Recognitions & Awards/Patents Issued

1. Huang, C., T-Raissi, A., Muradov, N.Z. "Solar Metal Sulfate – Ammonia Based Thermochemical Water Splitting Cycle for Hydrogen Production," UCF-645, Patent pending before USPTO.

FY 2010 Publications/Presentations

1. Huang, C., T-Raissi, A., Choi, P., Muradov, N.Z. "Hydrogen Production via Electrolysis of Aqueous Ammonium Sulfite Solution," paper presented at the 18th World Hydrogen Energy Conference, Essen, Germany, May 16–21, 2010.

2. Taylor, R., T-Raissi, A., Fenton S., Davenport, R., Symons, P. Presentation at the STCH Technical Progress Meeting, Florida Solar Energy Center, Cocoa, FL, March 23–24, 2010. (PowerPoint presentation).

3. Taylor, R., T-Raissi, A., Fenton S., Davenport, R., Genders, D. Presentation at Phase 1 Go/No-Go Meeting, DOE Golden Field Office, December 3, 2009 (PowerPoint presentation and Meeting Summary).

4. T-Raissi, A. "Thermochemical Water-Splitting Cycles for Hydrogen Production," Chapter in Energy Production and Storage – Inorganic Chemical Strategies for a Warming World, Encyclopedia of Inorganic Chemistry, R.H. Crabtree, Editor. *John Wiley & Sons Ltd*., 2010, in press.

5. Taylor, R., Davenport, R., T-Raissi, A., Muradov, N., Huang, C., Fenton, S. "Solar Thermochemical Hydrogen Production via a Sulfur-Ammonia Cycle," *SolarPACES 2009 Conference*, Berlin, Germany, September, 2009.

6. Davenport, R., Taylor, R. "Low Cost Glass-Reinforced Concrete Heliostats," *SolarPACES 2009 Conference*, Berlin, Germany, September, 2009.

7. Yao, W., Huang, C., Muradov, N.Z., T-Raissi, A. "Photocatalytic H2 Evolution on Visible Light Illuminated CdS Supported Pd-Cr2O3 Nanocomposite Cocatalyst Using Re-generable Sacrificial Donor," Submitted for publication in *JACS*.

8. Huang, C., Linkous, C.A., Adebiyi, O., T-Raissi, A. "Hydrogen Production via Photolytic Oxidation of Aqueous Sodium Sulfite Solutions," to appear in the *J. Environmental Science & Technology*.

9. Mao, L., T-Raissi, A., Huang, C., Muradov, N.Z. "Thermal Decomposition of (NH4) 2SO4 in the Presence of Mn3O4," to appear in the *Int. J. Hydrogen Energy*.

10. Yao, W., Huang, C., Muradov, N.Z., T-Raissi, A. "Photocatalytic H_2 Evolution on Visible Light Illuminated CdS Supported Pd-Cr_2O_3 Nanocomposite Cocatalyst Using Regenerable Sacrificial Donor," Paper submitted to the *J. of the American Chemical Society*.