

Solar-Driven Photocatalytically-Assisted Water Splitting

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PD14

Overview

Timeline

- Start date: Sept. 2007
- End date: Oct. 2011
- Percent complete: 15%

Budget

- Total project funding
 - DOE share: \$4M
 - Contractor share: \$1M
- \$300k received in FY07
- Funding for FY08: \$1M

Barriers

- Barriers addressed
 - U. High-Temperature Thermochemical Technology
 - V. High-Temperature Robust Materials
 - W. Concentrated Solar Energy Capital Cost
 - X. Coupling Concentrated Solar Energy & Thermochemical Cycles
- H₂ Production Target: **\$3.00/kg**

Partners

Project lead:

Solar System
Development

- FSEC at UCF
Reactor/Receiver &
Process Development



Objectives

- Evaluate photo/thermo-chemical water splitting cycles that employ the visible portion of the solar spectrum for production of hydrogen
- Select a cycle that has the best potential for cost-effective production of hydrogen from water – DOE target of **\$3.00/kg H₂**
- Demonstrate technical feasibility of the selected cycle using solar input in a bench-scale reactor
- Demonstrate pre-commercial feasibility via a fully-integrated pilot-scale solar hydrogen production system
- Perform economic analysis of the selected cycle.

Project Participants

- Science Applications International Corp.
 - Contract Management
 - Solar Concentration System Development & System Integration
- Florida Solar Energy Center at UCF
 - Photo/Thermo-Chemical Cycle Evaluation/Selection
 - Reactor/Receiver & System Design
- IPHE partnership

Project Phases

- PHASE 1: Sub-cycle testing & evaluation
- PHASE 2: Bench-scale testing of the complete cycle & pilot plant design
- PHASE 3: Pilot-scale demonstration

Milestones, Schedule & Deliverables

Month-Year	Type	Description	Status
Sep '08	Report	Select preferred water-splitting cycle, based on cost & performance evaluations	Complete
Sep '08	Report	Preliminary design of solar concentrator for pilot-scale test system	ongoing
Mar '09	Report	Summary of experimental results & economic analysis, with H ₂ cost estimate & recommendations for bench scale system	ongoing
Mar '09	GO/ NO-GO To Phase 2	Optimal high temperature water-splitting cycle selected for bench-scale testing & non-federal cost share in place for Phase 2	
Mar '10	Report	Summary of bench-scale reactor & solar system test results	
Mar '10	GO/ NO-GO To Phase 3	Bench-scale results prove to be technologically feasible to support scale-up to pilot-scale demonstration & reveal no major technical hurdles Economic analysis shows that the projected cost of hydrogen from this technology will meet 2010 target of < \$3/kg	
Sep '10	Report	Design of pilot-scale solar concentrator & pilot-scale receiver/reactor	
Apr '11	Report	Completion of concentrator installation; demonstration of dish operation with receiver	
Sep '11	Report	Final report with results of all testing and development, final cost estimates, & recommendations for further development	

Phase 1 Approach

- Sub-cycle Testing & Evaluation
 - Photo/Thermo-Chemical Cycle Analysis
 - Lab Testing of Selected Cycle
 - Report - Preferred Cycle Selection
 - Reactor/Process Configuration
- Solar Concentrator Design
 - Concentrator Specifications
 - Preliminary Concentrator Design
 - Subsystem Tests
 - Report - Prelim. Solar Concentrator Design
- Economic Evaluation

Technical Accomplishments/ Progress/Results

- Completed cycle analyses
- Selected cycle for further development
- Validated hydrogen production photo-process
- Validated oxygen production sub-cycle chemistry
- Evaluated reactor/receiver options
- Evaluated solar collector configurations

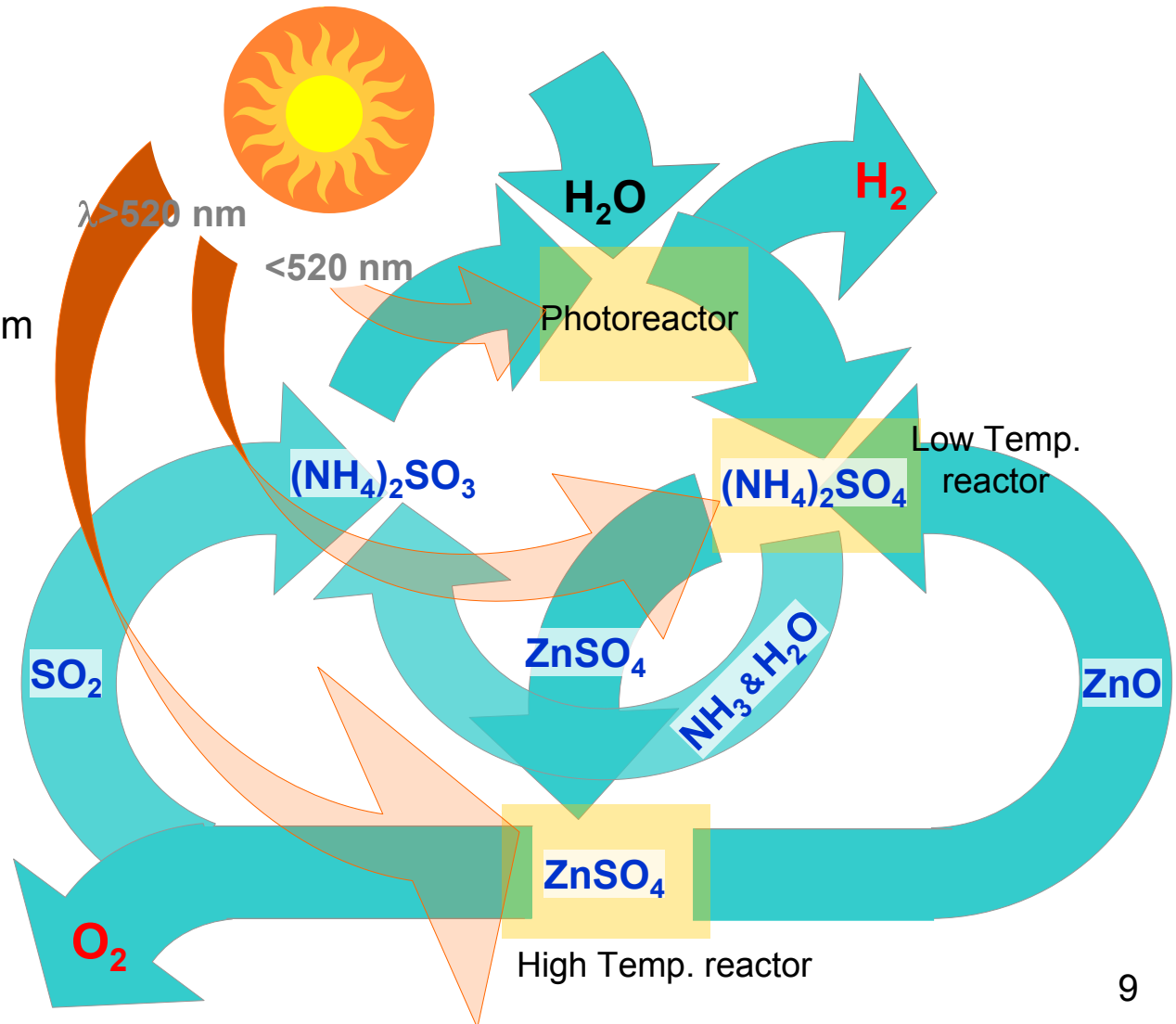
S-NH₃ Solar Water Splitting Cycle

H₂ Production Step

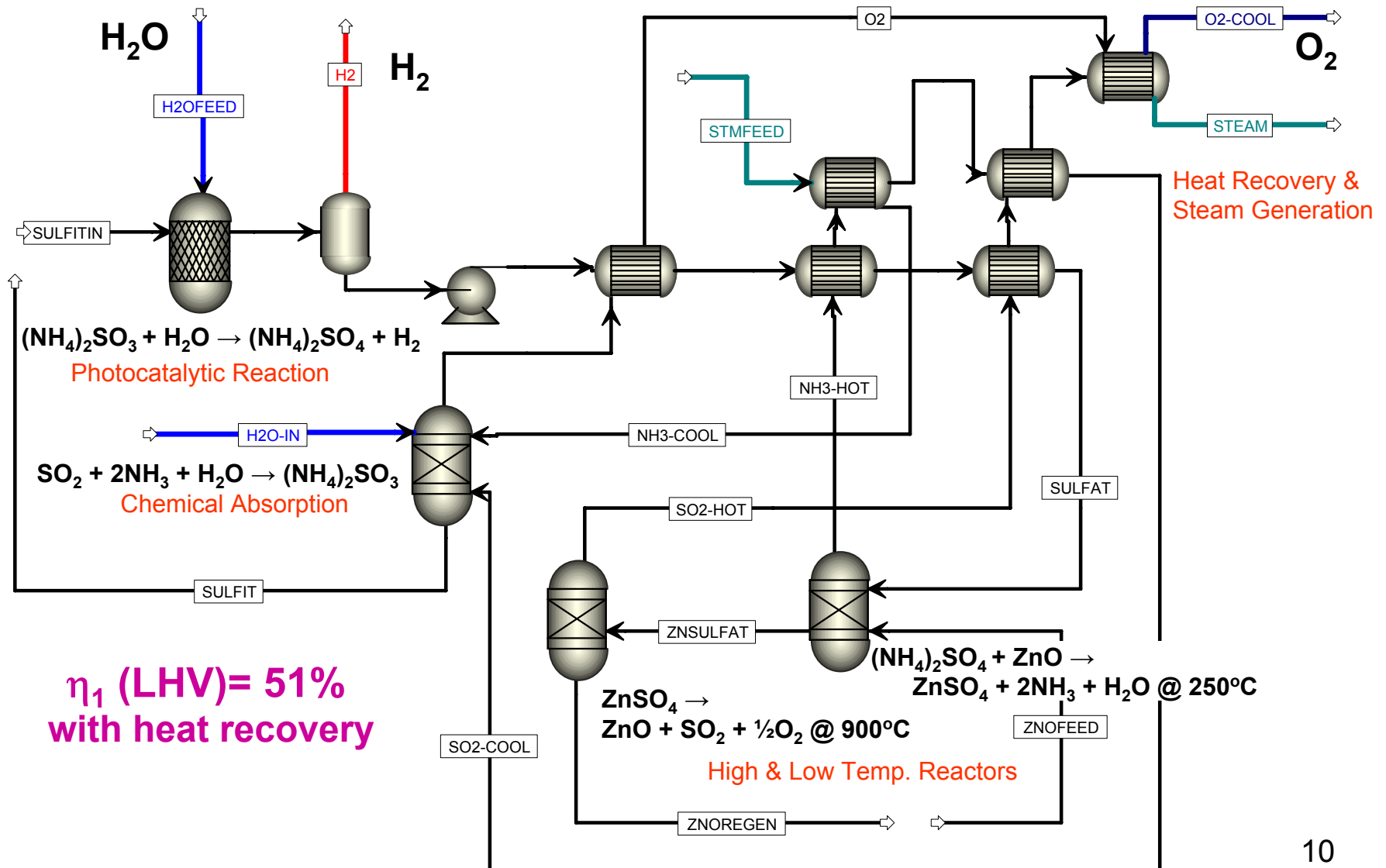
- Photocatalytic
- Operates at $\lambda < 520$ nm
- Requires ~20% of solar spectrum

O₂ Production Process

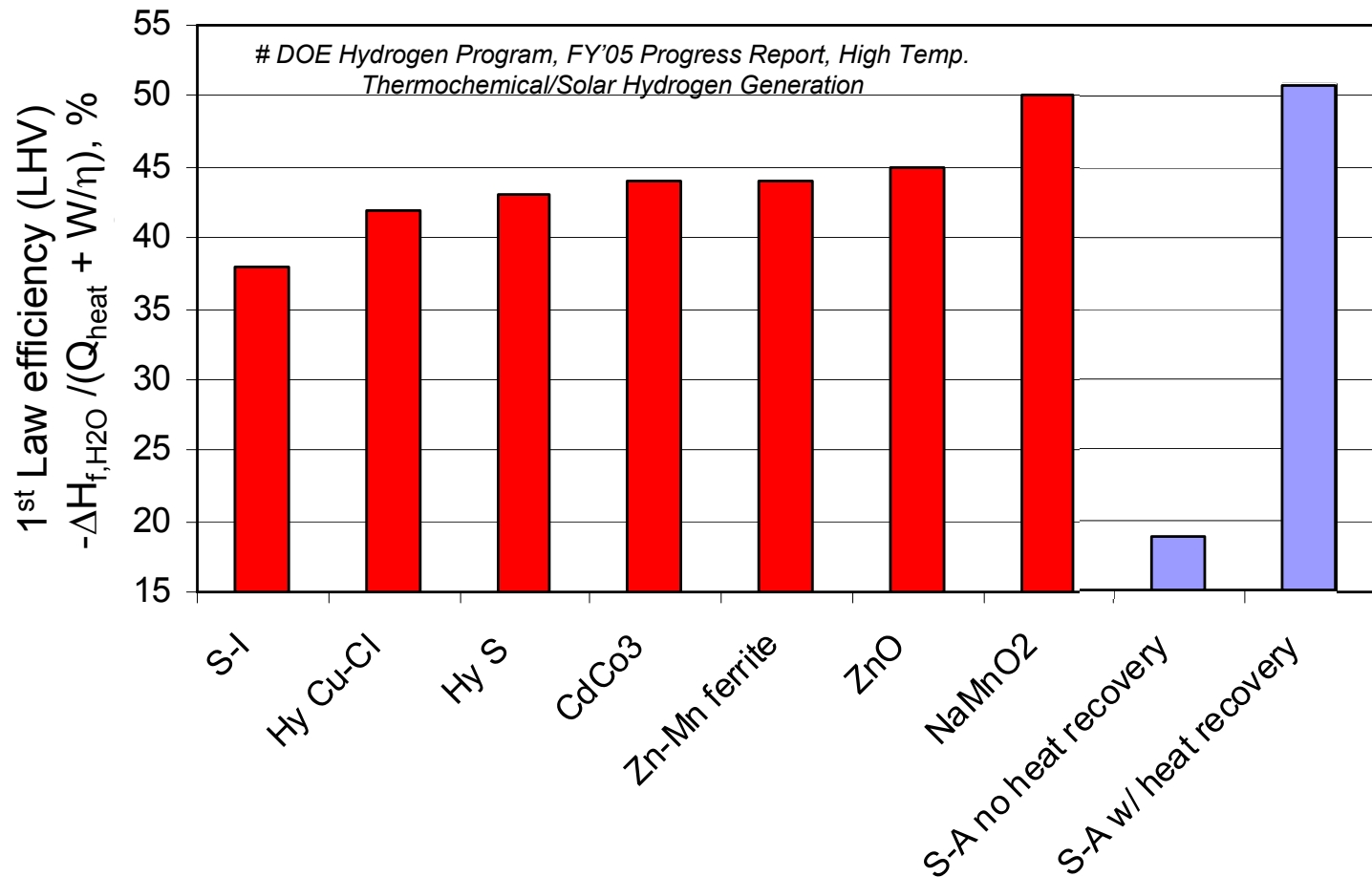
- Thermocatalytic
- Operates at $\lambda > 520$ nm
- Requires ~80% of solar spectrum



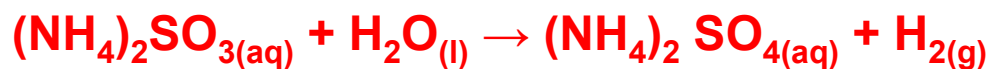
Aspen Flowsheet of S-NH₃ Cycle



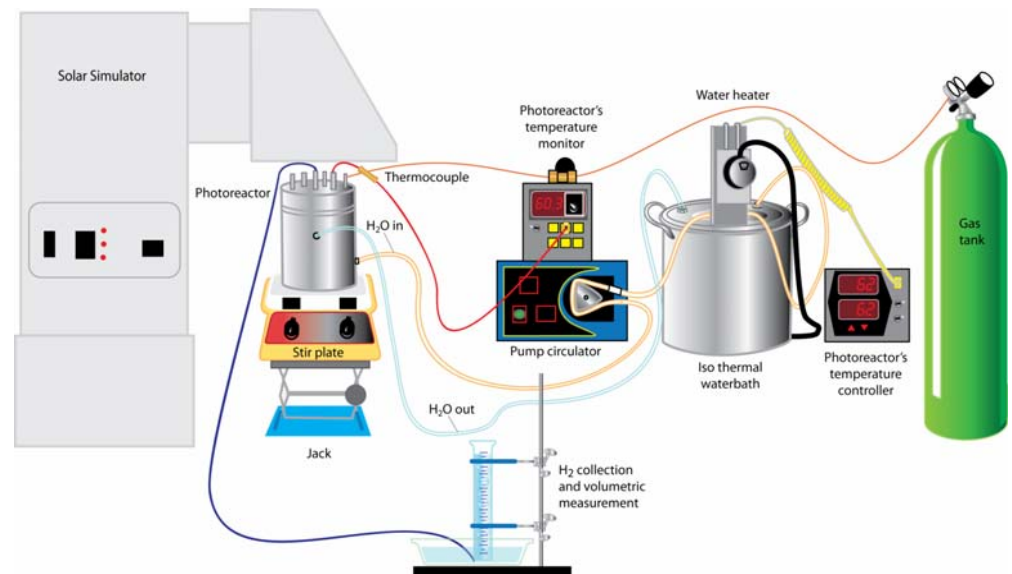
Comparison of S-NH₃ Cycle Efficiency to Other HT Cycles[#]



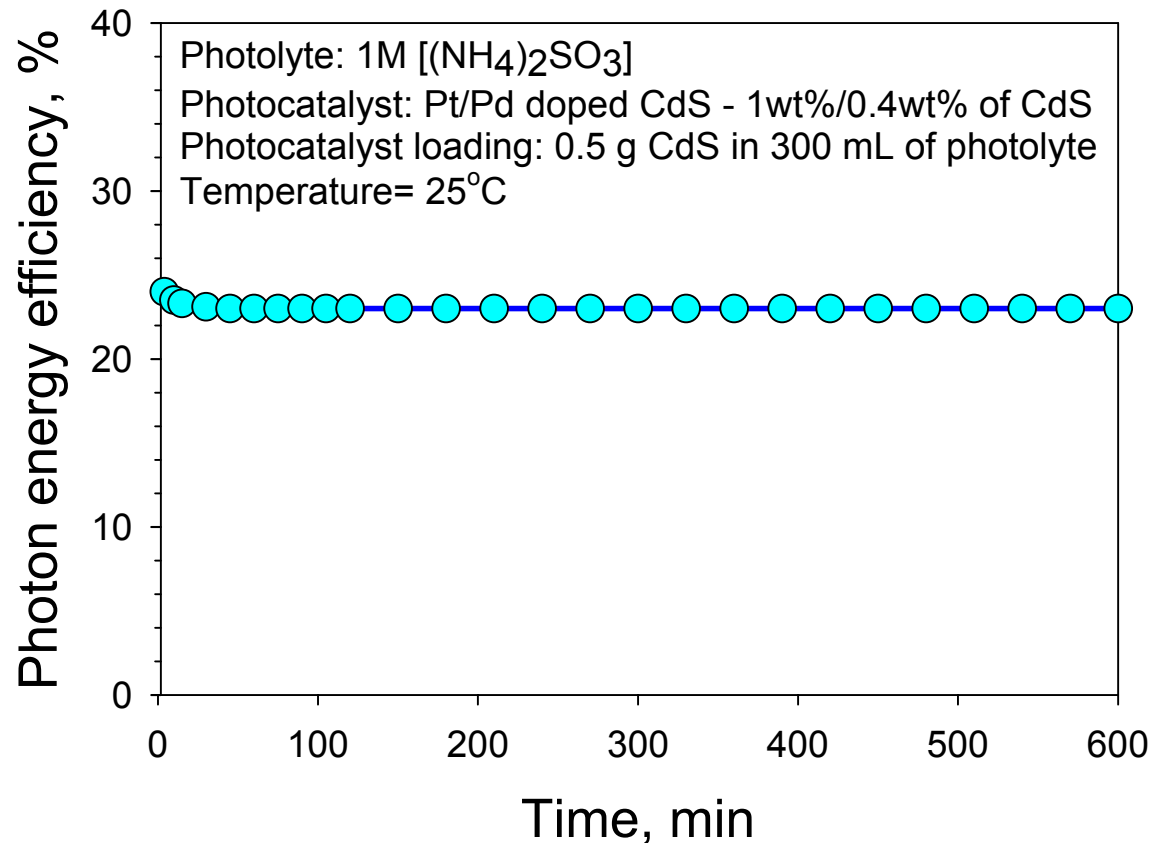
Photocatalyst Screening for Hydrogen Production



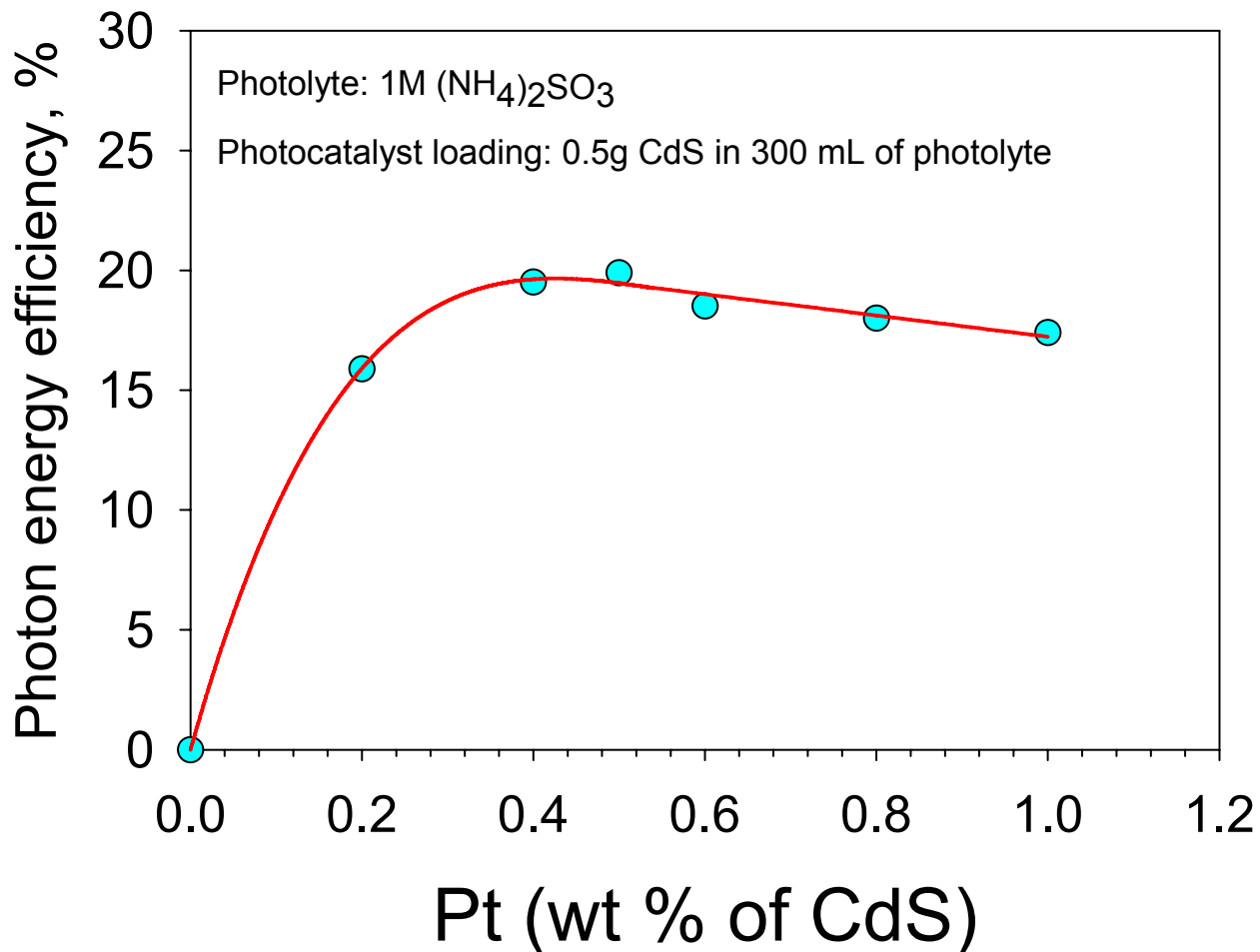
Setup for Photocatalytic H₂ Production Experiments



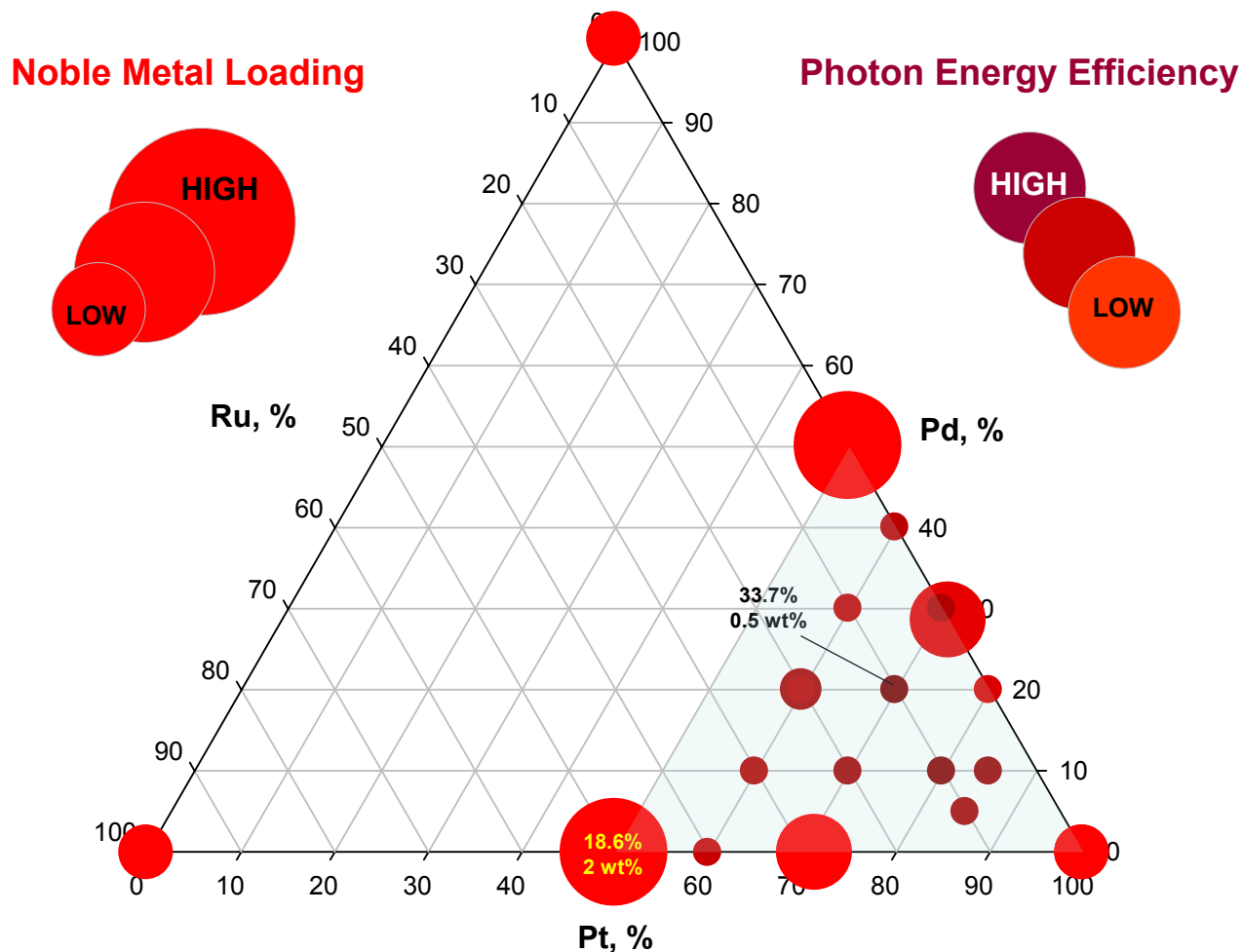
Stability of the Photosystem in Hydrogen Generation Step



Photon Efficiency as a Function of Single Metal Dopant Loading

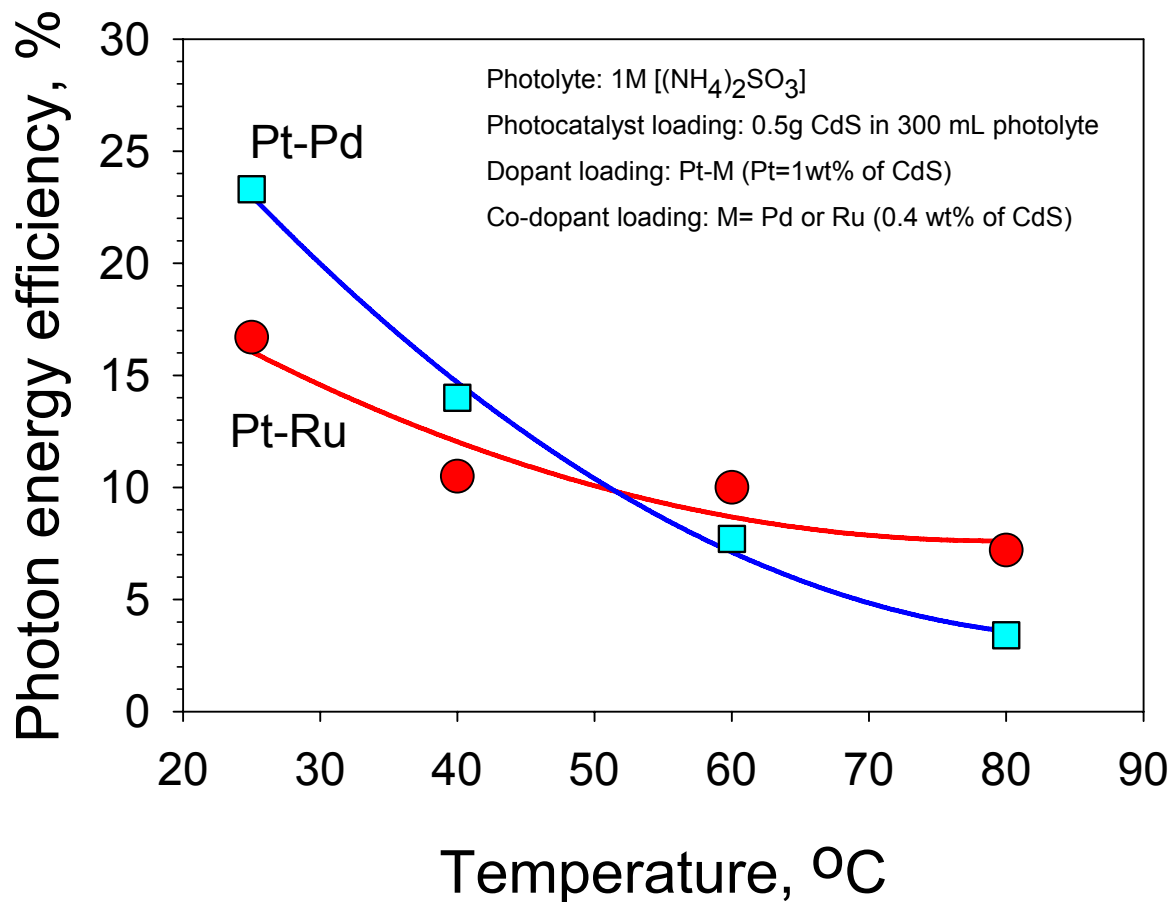


Effect of Photocatalyst Doping

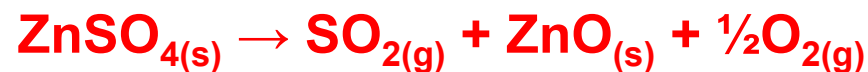


Photocatalyst loading: 0.5 g CdS in 300 mL photolyte: 1M $(\text{NH}_4)_2\text{SO}_3$

Effect of Photolyte Temperature



Sub-Cycle for Oxygen Production



Experimental Methodology

Investigated thermocatalytic decomposition of:

- Pure $(\text{NH}_4)_2\text{SO}_4$
- $\text{ZnO}:(\text{NH}_4)_2\text{SO}_4 = 1.5:1$ (molar ratio)
- ZnSO_4

In the temperature range of 100°C-900°C.

Employing following analytical techniques:

- TG-DTA
- TPD-MS
- GC-MS/UV-Vis

Thermocatalytic Decomposition of $(\text{NH}_4)_2\text{SO}_4/\text{ZnO}$ – Summary of Reaction Product Analysis

T/ °C Method	100	200	300	400	500	600	700	800
TGA-MS				NH ₃		SO ₃		
				H ₂ O				
GC-MS/UV-Vis						NH ₃		SO ₃
						H ₂ O		SO ₂
TPD-MS				NH ₃				O ₂
				H ₂ O				SO ₂
								SO ₃

ZnO/(NH₄)₂SO₄ Thermocatalytic Decomposition – Reaction Mechanisms

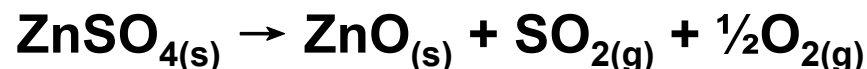
Step 1 (T < ~400°C):



Step 2 (T < ~800°C):



Step 3 (T > ~800°C):



Solar Hydrogen Production

Heliostat Cost Reduction

Heliostats are the largest single cost component in the solar hydrogen production system

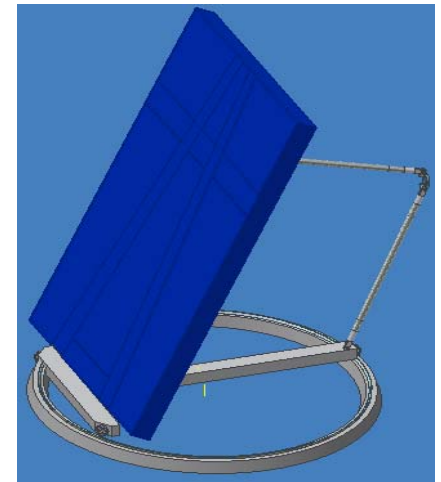
Identified potential for cost savings using a GRC (Glass-Reinforced Concrete) heliostat structure :

- Very low cost material (\$0.15/kg)
- Easy to process (automated spray on mold)
- Excellent weathering and stiffness
- Excellent design flexibility (molded-in reinforcing ribs and mounts; pre-tensioning is possible)



Preliminary design:

- Small (10-15 m²) heliostat, factory-produced, PV self-powered, with wireless communication to minimize field wiring costs
- Factory-made, surface-installed concrete track foundation to simplify installation

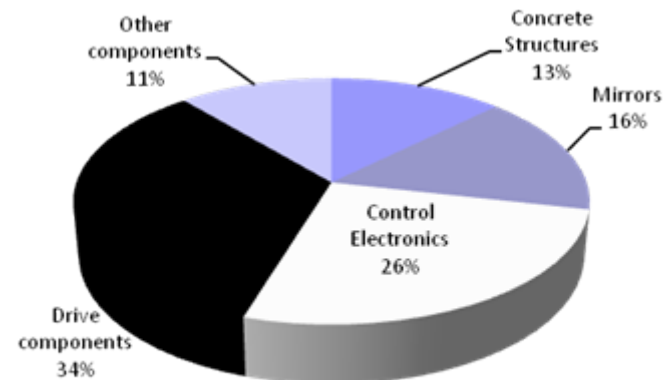


Solar Hydrogen Production

Preliminary System Comparison

	Area of Solar Reflectors [sq.km]	Land area [sq.km]	Total Capital Cost [\$M]	Cost of Hydrogen [\$/kg]
Baseline Hybrid Sulfur (HyS) System (Kolb): Heliostat/Central Receiver	1.30	6.50	381.2	3.00
Dish concentrator	0.85	3.42	409.2	3.13
FSEC S-NH₃ Cycle w/ Solar Boost:				
Dish concentrators w/cold mirror	0.83	3.33	644.3	3.33
Heliostat w/hot mirror	1.06	5.31	810.6	4.12
Heliostat-separate photoreactor	0.84	5.90	435.1	2.33
Advanced GRC Heliostat-separate rxr	0.84	5.90	417.4	2.25

- **Results:**
 - **FSEC process hydrogen cost <\$3/kg**
 - Hot/cold mirror systems more expensive
 - FSEC process with separate photoreactor shows cost advantage over baseline (HyS)
 - Advanced heliostat improves costs further
- GRC prototype heliostat cost estimated at 17% less than conventional glass/metal heliostat (\$105/sq.m vs. \$126/sq.m)



Future Work

- Close & complete analyses of S-NH₃ cycle
- Complete H₂ production photocatalyst screening
- Reduce noble metal loading on the photocatalyst
- Develop immobilized photocatalyst formulations
- Conclude oxygen production process optimization
- Analyze & design the high temperature reactor/receiver system
- Complete solar collector system analysis & design
- Perform technoeconomic & H₂A analysis of the S-NH₃ cycle

Summary

- S-NH₃ photo/thermochemical water splitting cycle has been validated for solar hydrogen production
- S-NH₃ cycle utilizes the thermal portion of solar spectrum for the production of O₂ while the high energy photonic part of sunlight is used for hydrogen generation
- The 1st law efficiency of the S-NH₃ cycle was calculated using Aspen flowsheeting & shown to be **51%**
- A large number of doped & polymer stabilized CdS based photocatalysts have been synthesized and evaluated for H₂ production from aqueous ammonium sulfite solutions
- Heliostat field appears to be the preferred solar concentrator approach
- GRC shows promise to lower heliostat field costs