

Solar High-Temperature Water Splitting Cycle with Quantum Boost

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Science Applications International Corp. –
San Diego, California

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PD027

Overview

Timeline

- Start date: 09/01/2007
- End date: 10/30/2012
- Percent complete: 40%

Budget

- Total project funding
 - DOE share: \$4M
 - Contractor share: \$1M
 - Actual Exp. FY09: \$718k
 - Exp. to date FY10: \$358k
- Note: Funding shown for FY09 and FY10 are actual expenditures of DOE funds rather than DOE obligations

Barriers

- U. High-Temperature Thermochemical Technology
- V. High-Temperature Robust Materials
- W. Concentrated Solar Energy Capital Cost
- X. Coupling Concentrated Solar Energy & Thermochemical Cycles
 - 2017 H₂ Production Target: \$3.00/kg
 - 2017 Cycle Efficiency Target: >35%

Partners

- SAIC (Lead)
Solar System/Receiver
- UCF-FSEC
Thermochemical Process
- Electrosynthesis
Salt electrolysis



Project Objectives

- RD&D of the Viability of a New & Improved Sulfur Family Thermochemical Water-Splitting Cycle (i.e., sulfur-ammonia, S-A) for large-scale hydrogen production using solar energy
- More Specifically, Overall Project Goals are to:
 - Evaluate S-A water-splitting cycles that employ photocatalytic or electrolytic hydrogen evolution steps and perform lab testing to demonstrate feasibility of the chemistry
 - Perform economic analyses of S-A cycles as they evolve
 - Select a cycle that has high potential for meeting the DOE 2017 cost target of \$3/kg hydrogen and efficiency goal of >35%
 - Demonstrate technical feasibility of the selected S-A cycle in bench-scale, closed-loop tests
 - Demonstrate pre-commercial feasibility by testing and evaluation of a fully-integrated pilot-scale closed-cycle solar hydrogen production plant

Past Year Project Objectives

- **Electrolytic Hydrogen Production Advancement**
 - Reduce cell voltage below 1 volt by increasing temperature/pressure, controlling pH, improving cell design
 - Find conditions where anode can be run at high pH without adverse effects
 - Investigate catalysts to reduce the over-potential and increase current density
- **Begin Oxygen Production Sub-Cycle Evaluation**
 - Determine if an all liquid K_2SO_4 sub-cycle is feasible
- **Perform H₂A economic analyses of modified S-A cycles**
 - Electrolytic H₂ production and K_2SO_4 oxygen production sub-cycles
- **Perform Solar Concentrating System and Receiver Evaluations to Ensure Feasible, Efficient and Cost Effective Interface with the Modified S-A Cycles**
 - Refine low cost heliostat design and prepare detailed production cost estimates

Impact on Program Barriers

- U. High-Temperature Thermochemical Technology – This project is developing a new sulfur family thermochemical cycle that is intended to operate at lower temperatures and be more cost effective than other S-family cycles
- High-Temperature Robust Materials – Materials better able to operate in the high temperatures and caustic environment of the receivers and reactors are being developed.
- W. Concentrated Solar Energy Capital Cost – Heliostat field cost is being reduced by consideration of a new design for heliostats, and whole-system costs are being reduced by optimizing the solar-chemical interface
- X. Coupling Concentrated Solar Energy & Thermochemical Cycles – The solar field and receivers are being evaluated and designed to provide appropriate amounts of energy at necessary temperature levels and with appropriate controls

Approach

- Identify Weaknesses of Existing Thermochemical Water-Splitting Cycles and Develop a new Sulfur-family Cycle with Fewer Phenomenological Hurdles
- Conduct Laboratory Evaluation of all Processes within the Cycle
- Develop Comprehensive AspenPlus Flowsheet(s) of the Cycle and Modifications
- Perform H2A Analysis of the Flowsheeted Cycle(s) to Compare Design and Operational Approaches
- Design Solar Collector Field to Complement Chemical Process and Maximize Solar/System Efficiency
- Refine Process with Improvements Suggested by Lab Testing, Solar Configuration Studies, and H2A/Aspen+ Analyses
- Perform Bench-Scale On-Sun Testing of Individual Chemical Processes, then Integrated Pilot-Scale Testing

Milestones

Past Milestones

- Selected a variant of the Westinghouse hybrid sulfur cycle for development, the Sulfur-Ammonia (SA) cycle
- Experimentally validated all reaction steps for the SA cycle
 - Photocatalytic H₂ production step
 - High-temperature step with zinc sulfate sub-cycle
 - Electrolytic H₂ production step validation initiated
- Initial conceptual design of solar concentrating system
- Low cost heliostat development initiated

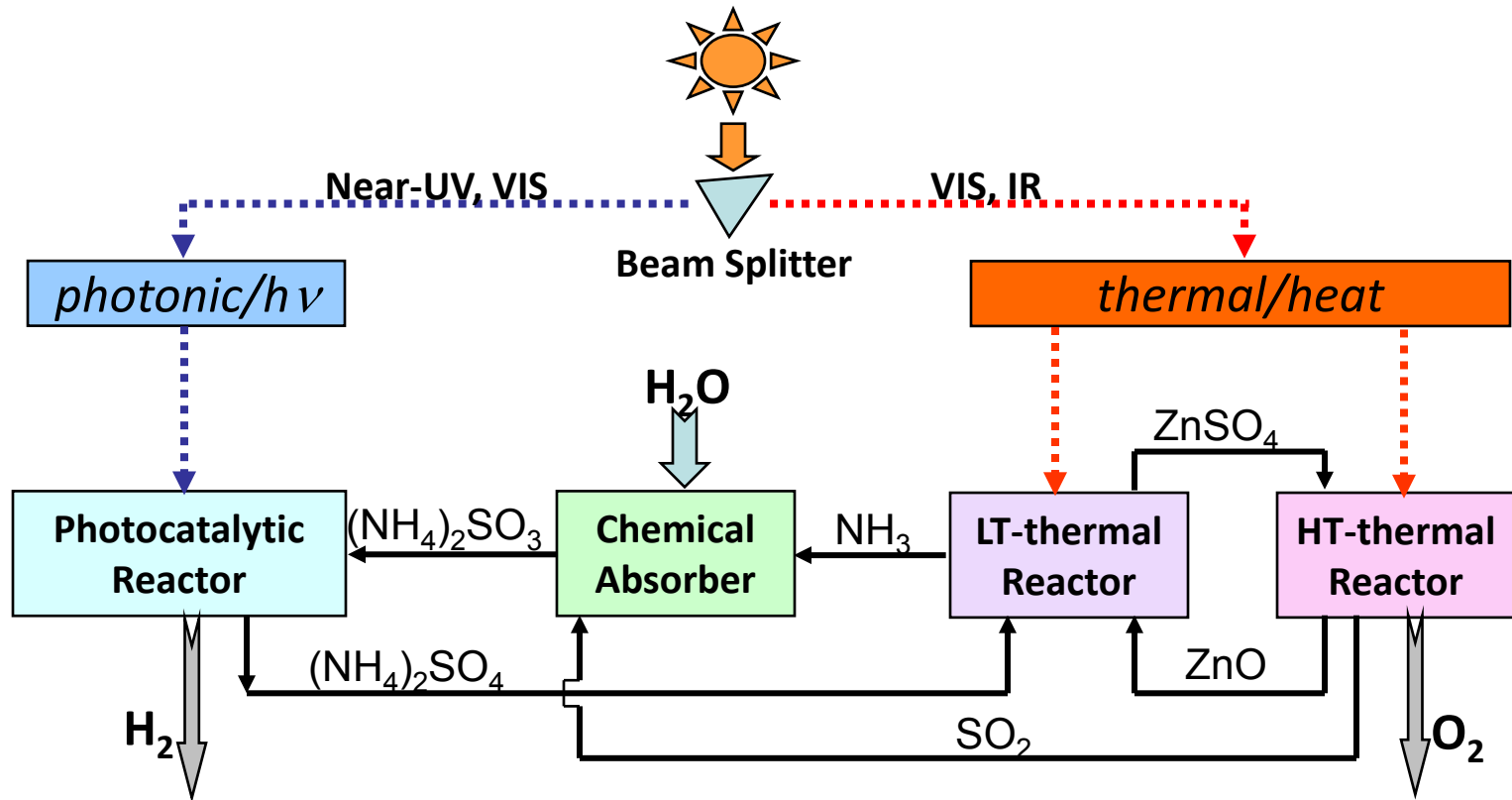
Current Milestones

- Electrolytic H₂ production step validation
- All-Liquid O₂ production step validation
- Verification of viable solar concentrating system

Contractual Milestones

- Zero funding for FY 2009 required stretching project resources from previous years
- Negotiating tasks and budget modification

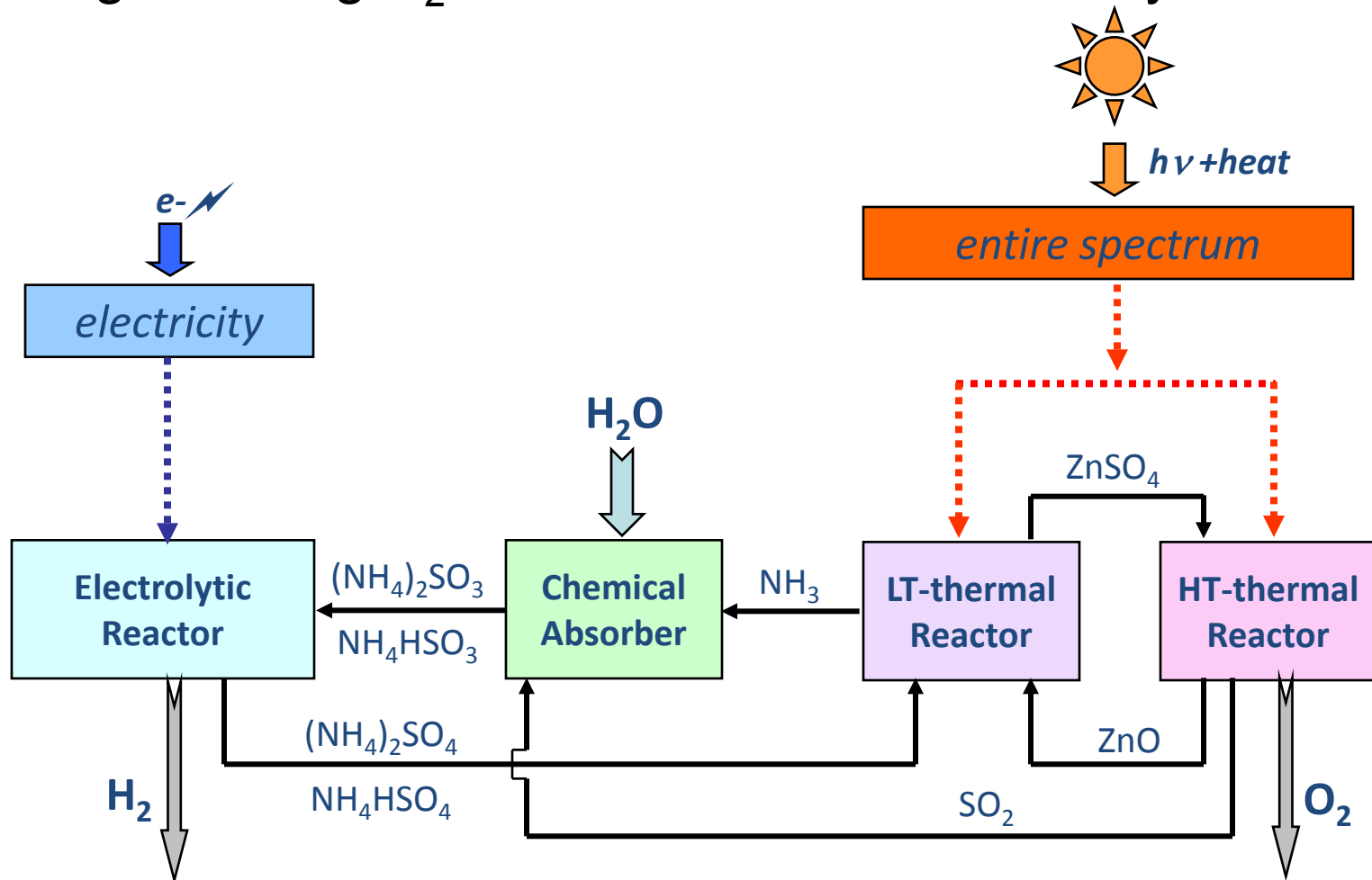
Cycle Review



- Original S-A Cycle Concept used a Photocatalytic Reaction to Oxidize Ammonium Sulfite and Release Hydrogen, and a High-Temperature Thermo-Chemical Regeneration Process
- Beam-Splitting Was Used to Separate Out just the Photo-Active Portion of the Solar Spectrum

Electrolytic SA Process

To reach efficiency goals, an electrolytic step for generating H_2 was introduced in the SA cycle



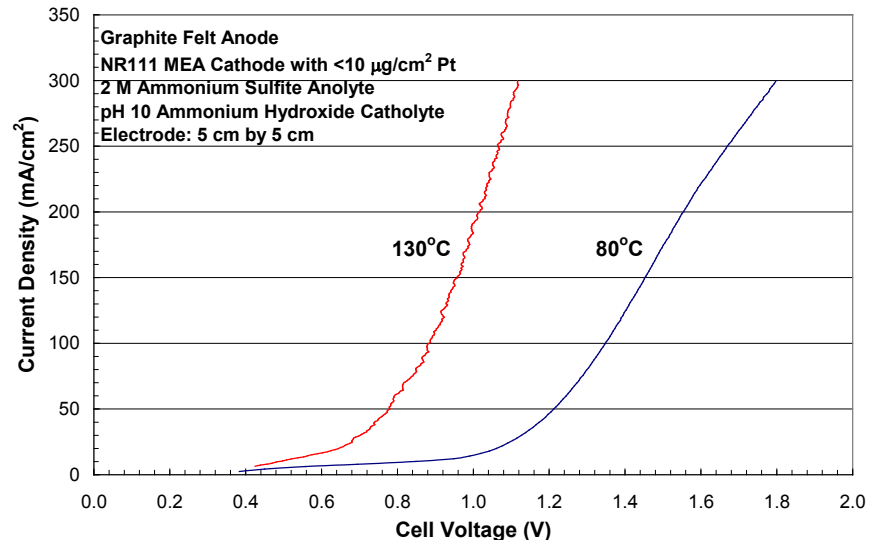
Electrolytic SA Process

- The least costly H₂ production scenario has the solar thermochemical plant run as a combined hydrogen and power generation facility with solar-supplied steam providing all (or nearly all) on-site electricity needs
- Electrosynthesis, with expertise in salt electrolysis, helped optimize the electrolytic process and cell design
- FSEC has pursued electrolytic cell development & optimization and is beginning detailed development of the complementary oxygen production half-cycle

Electrolysis Progress

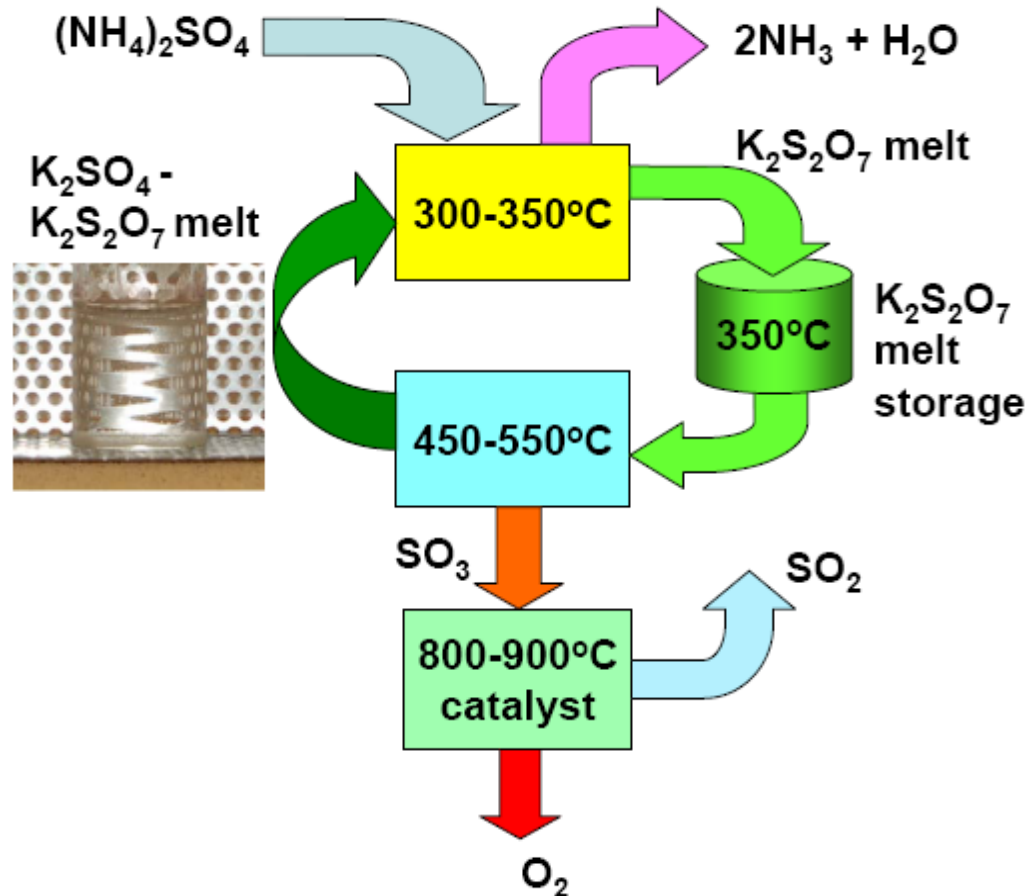
- Quantitative hydrogen production with efficient sulfite oxidation has been verified.
- Voltage of electrolytic cell reduced from 1.2V to less than 1.0V by increasing temperature/pressure, controlling pH, improving cell design
- FSEC recently reported achieving 0.63V at 186mA/sq.cm using proprietary new design/catalyst
- Working on further improvements to reduce cell voltage and increase current density. Goal is <0.5V at 400mA/sq.cm

Example data showing reduction in Voltage at 100mA/sq.cm from over 1.3V to <0.9V by running cell at elevated temperature. Further improvements are being pursued.



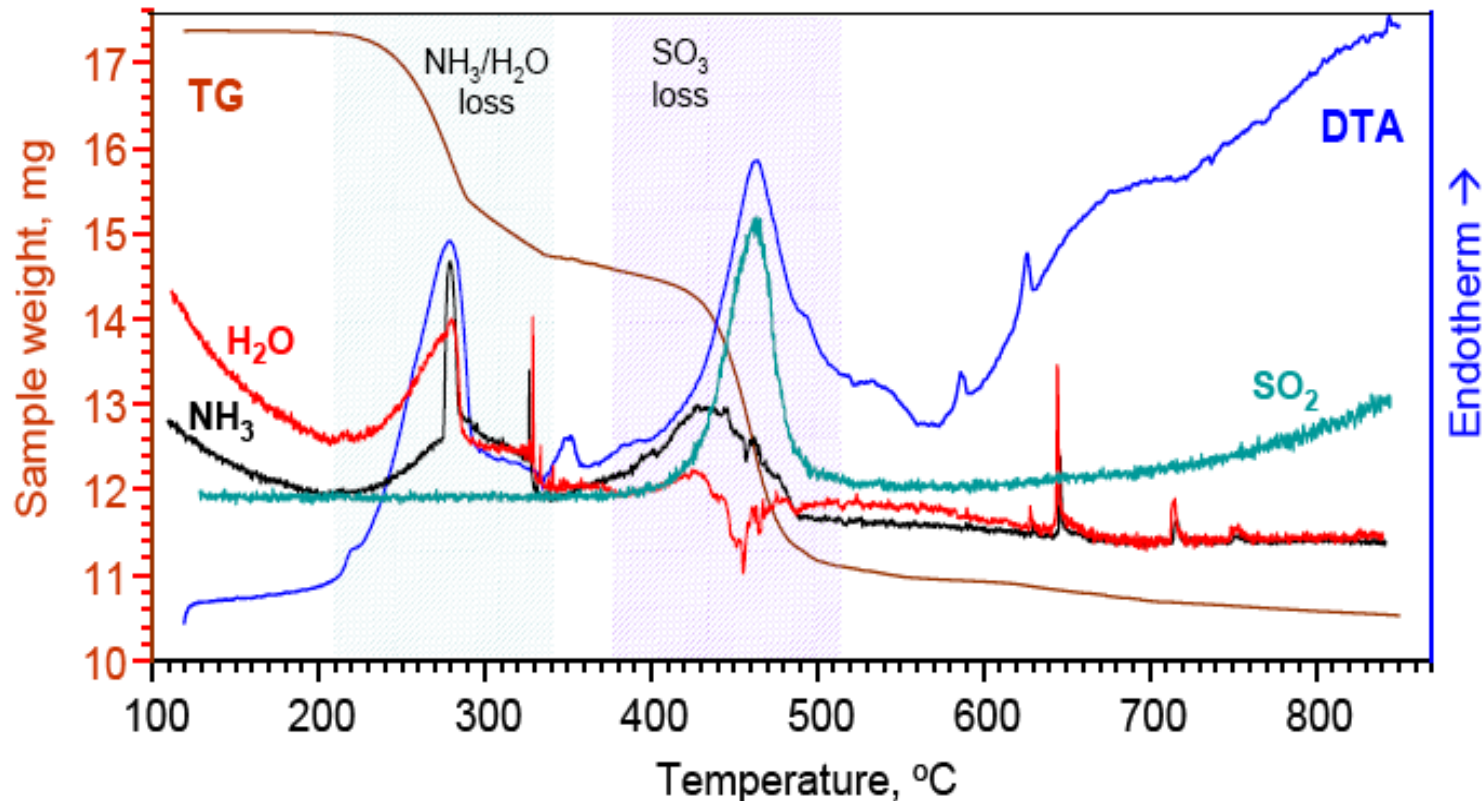
Oxygen Generation half-Cycle

- The All-(Liquid/Gas) High-Temperature Sub-Cycle Using Potassium Sulfate Still Appears Feasible, but More Lab Testing is Needed

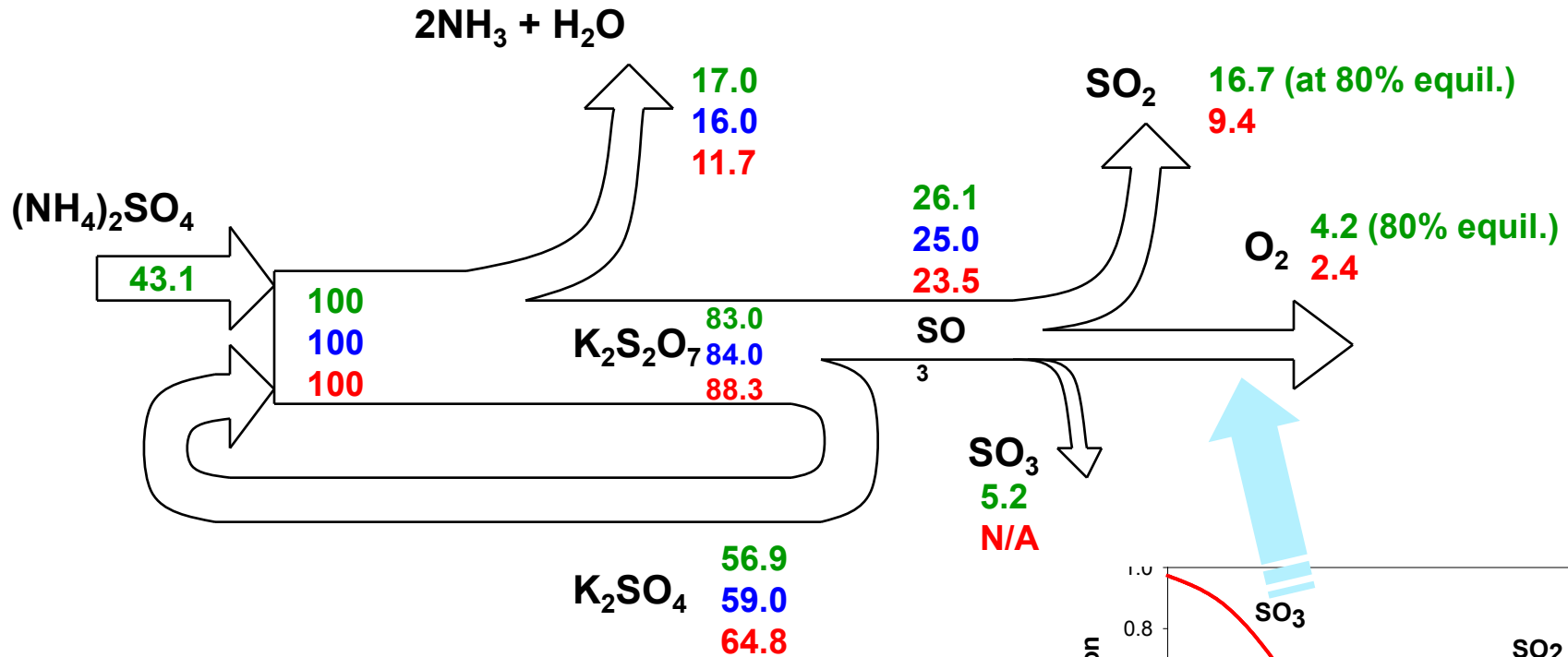


Oxygen Half-Cycle

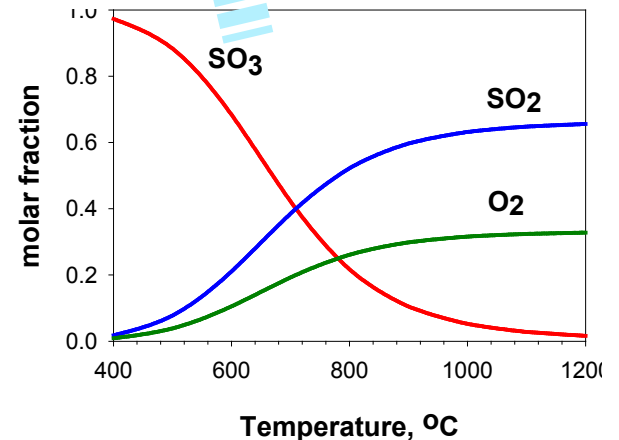
- TG/DTA-MS Analysis of Decomposition of $(\text{NH}_4)_2\text{SO}_4 - \text{K}_2\text{SO}_4$ Mixture (1.5:1.0 molar)
 - Ammonia, Water, and Sulfur Dioxide have been positively identified as the thermal decomposition products of the mixture



Mass Balance for the Oxygen Evolution Half-Cycle



Green: Theoretical
 Blue: TGA measurements
 Red: Reactor Experiments



Modeling and Economic Analysis

- Aspen+ Process Design and Analysis
 - Aspen+ analysis has been used to perform trade off studies and optimize the overall plant configuration, e.g.:
 - Electrical heating of sulfur trioxide reactor was shown to be not cost-effective compared to direct solar heating
 - Electrical production from steam and ammonia in process was shown to be sufficient to power electrolytic process
- H2A Economic Analysis
 - H2A analysis has been continuously updated as lab results were obtained and Aspen+ designs were refined

SA Cycle Analysis

Flowsheet development

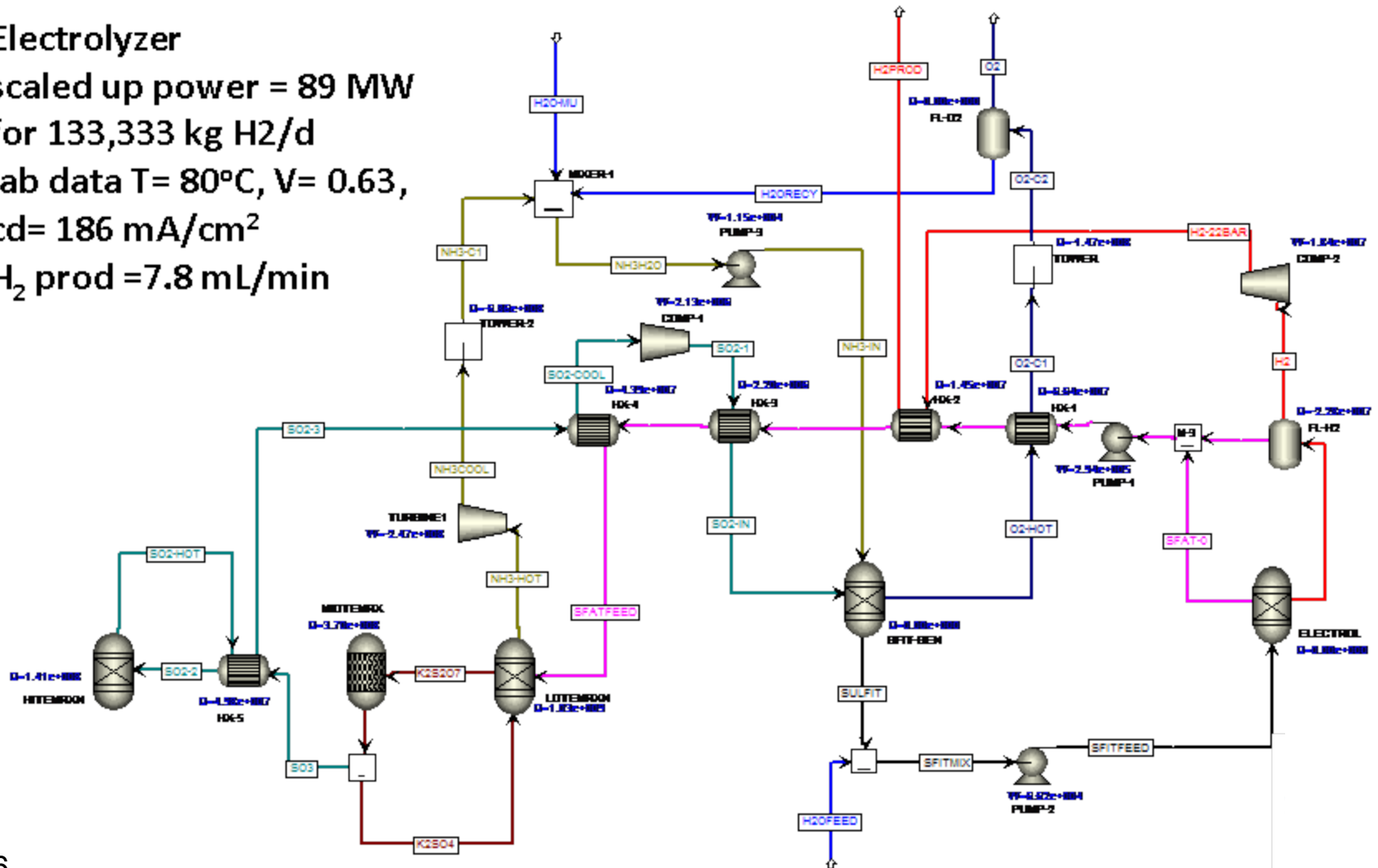
Electrolyzer

scaled up power = 89 MW
for 133,333 kg H₂/d

lab data T = 80°C, V = 0.63,

cd = 186 mA/cm²

H₂ prod = 7.8 mL/min

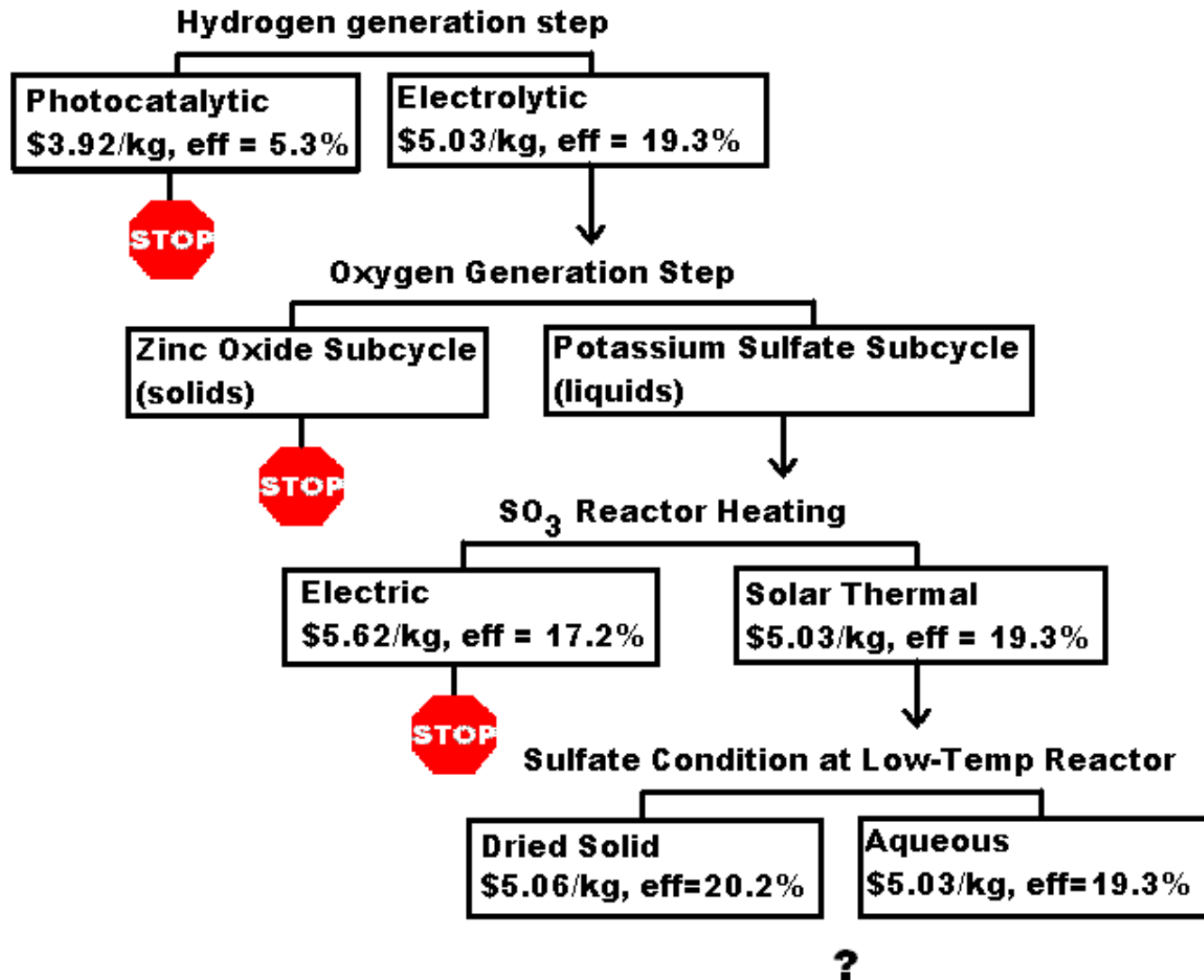


SA Cycle Comparison

Economics & Efficiency

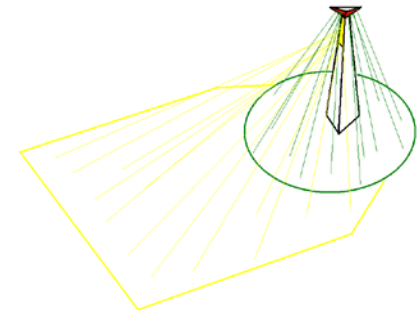
Description	Electrolysis = 89 MW solid am sftat to solar react electr & steam purchased		Electrolysis = 89 MW aq am sftat to solar react no electr or steam purchas		Photocatalytic aq am sftat to solar react no electr or steam purchas	
	Cost	%	Cost	%	Cost	%
Estimated Capital Cost M\$ (2005)						
Heliostat Field, Tower, & Receiver	\$410	60.8%	\$686	71.4%	\$686	69.5%
Land	\$6	1.0%	\$11	1.1%	\$11	1.1%
Electrolyzer/Photocat Reactor	\$130	19.3%	\$130	13.5%	\$158	16.0%
Chemicals	\$20	3.0%	\$20	2.1%	\$20	2.0%
Process Equipment	\$107	15.9%	\$113	11.8%	\$113	11.5%
Total	\$673	100.0%	\$960	100.0%	\$988	100.0%
H2A analysis \$/kg H2 produced						
Capital Cost	\$4.10		\$5.39		\$5.54	
Fixed O & M	\$0.70		\$0.92		\$1.06	
ByProduct Credits	\$0.00		-\$0.34		-\$1.56	
other variable costs incldg utilities	\$1.41		\$0.01		\$0.01	
Total	\$6.21		\$5.98		\$5.05	
Overall Efficiency (%)	20.2		19.3		5.2	

Summary of Trade-offs/Decision Points



Solar Field Development

- Solar Field Design and Analysis
 - Helio­stat field model was refined for performing conceptual design studies
 - Estimates annual production at Barstow, CA conditions (using hourly TMY data)
 - Includes effects of field density, atmospheric attenuation, etc.
 - Model used to evaluate multiple helio­stat field configurations as the chemical process has evolved
 - All-liquid high-temperature system opens door for use of dish concentrators rather than helio­stat field
 - Molten salt storage makes 24/7 operation feasible
- Helio­stat Development
 - Prototype 1/2-scale helio­stat with GRC structure was tested by SAIC, demonstrating fabrication, installation, and operational features
 - Projected installed helio­stat cost is less than \$90/sq.m. (vs. \$126/sq.m.) at low production; further cost reduction at higher production



Project Partners

Science Applications International Corp. – Prime Contractor (Industry)

- Project management & system integration
- Solar concentrator/receiver evaluation & design
- Economic evaluation & hydrogen production cost estimates

UCF/Florida Solar Energy Center (FSEC) – Subcontractor (Academia)

- Thermochemical cycle evaluation & development
- Electrolytic cell development
- Chemical Plant Analysis
- Thermal reactor design & optimization

Electrosynthesis Company, Inc. – Subcontractor (Industry)

- Salt electrolysis expertise
- Electrolytic cell development & optimization

FY10/FY11 Activities

- Complete Optimization of Electrolytic Oxidation Process
 - Test at higher temp (130°C) & higher pressure (2 bar) regimes
 - Incorporate better catalysts that lower the over-potential at the anode & allow operation at high current densities
 - Maintain pH at anode and cathode to avoid formation of reduced sulfur species
 - Continue to improve cell design, including undivided cells or alternate micro-porous separators
- Complete Evaluation of High-Temperature K_2SO_4 Sub-Cycle
 - Screen prospective catalysts for sulfur trioxide decomposition
 - Study phase equilibrium and identify favorable conditions for the process
 - Optimization of process parameters and identification of side reactions and by-products
- Economic and Solar System Analysis
 - Continued Refinement of the Solar Field, Aspen+, and H2A Analyses to Incorporate Chemical Process Modifications
 - Evaluation of receiver materials, storage and control strategies

Summary

- **Electrolytic SA Cycle Step**
 - This is the next step on the critical path
 - Progress is being made on reducing voltage and increasing current density in electrolytic cells and needs to continue
 - Cell design refinement and catalyst research are continuing
- **All-Liquid High-Temperature Oxygen Generation**
 - Initial lab results prove the subcycle feasibility
 - Optimization of process and integration into viable solar concentrating system and receivers needs to be evaluated
- **Aspen+ and H2A Continue to be Used to Optimize and Trade-off SA Cycle Configurations**
- **Next-Phase Program is Designed to Show the Electrolytic Hydrogen Production Approach Can Meet Cost Goals, Demonstrate Oxygen Cycle Feasibility in Lab Tests, and Validate Solar System Compatibility so the SA Cycle Can Proceed to Bench-Scale On-Sun Tests**

Supplemental Slides

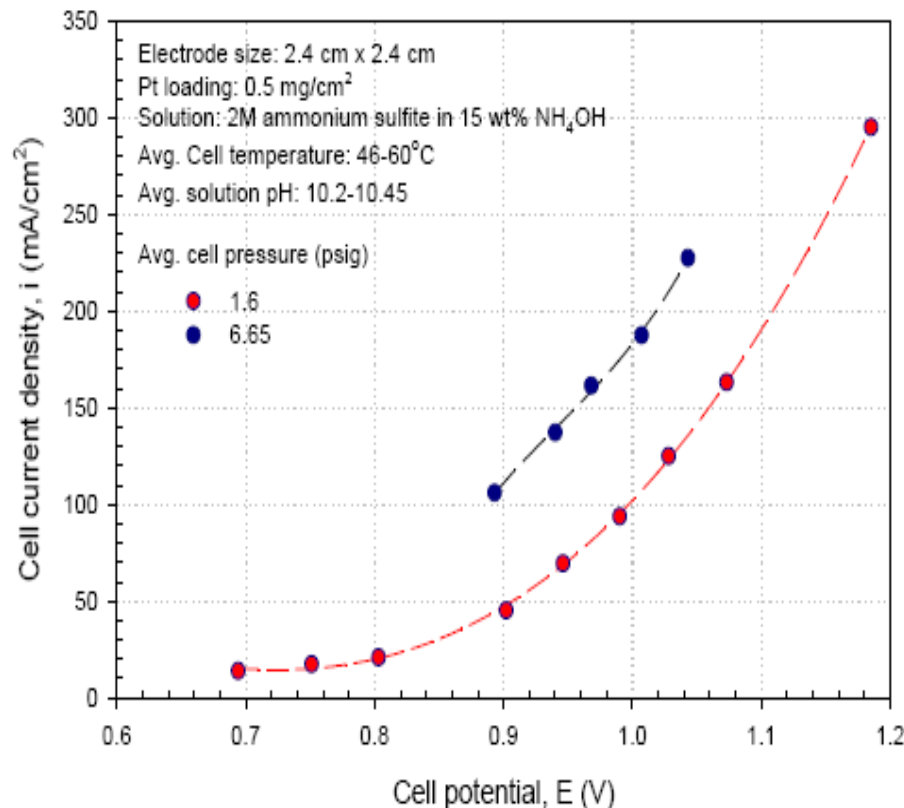
Electrolytic SA

– Earlier Exp. Observations

- Main source of voltage loss was on the anode side
 - May need to explore higher temp (130°C) & higher P (2 bar) approach
 - Some improvements may be obtained by using conditions where anode can be operated at high pH by
 - Reintroducing ammonia from catholyte into anolyte
 - Exploring the use of undivided cells or use of alternate microporous separators
 - Maintain alkaline pH at the cathode to prevent sulfite reduction
 - Need catalysts that lower the over-potential at the anode & allow operation at high current densities

Electrolytic SA

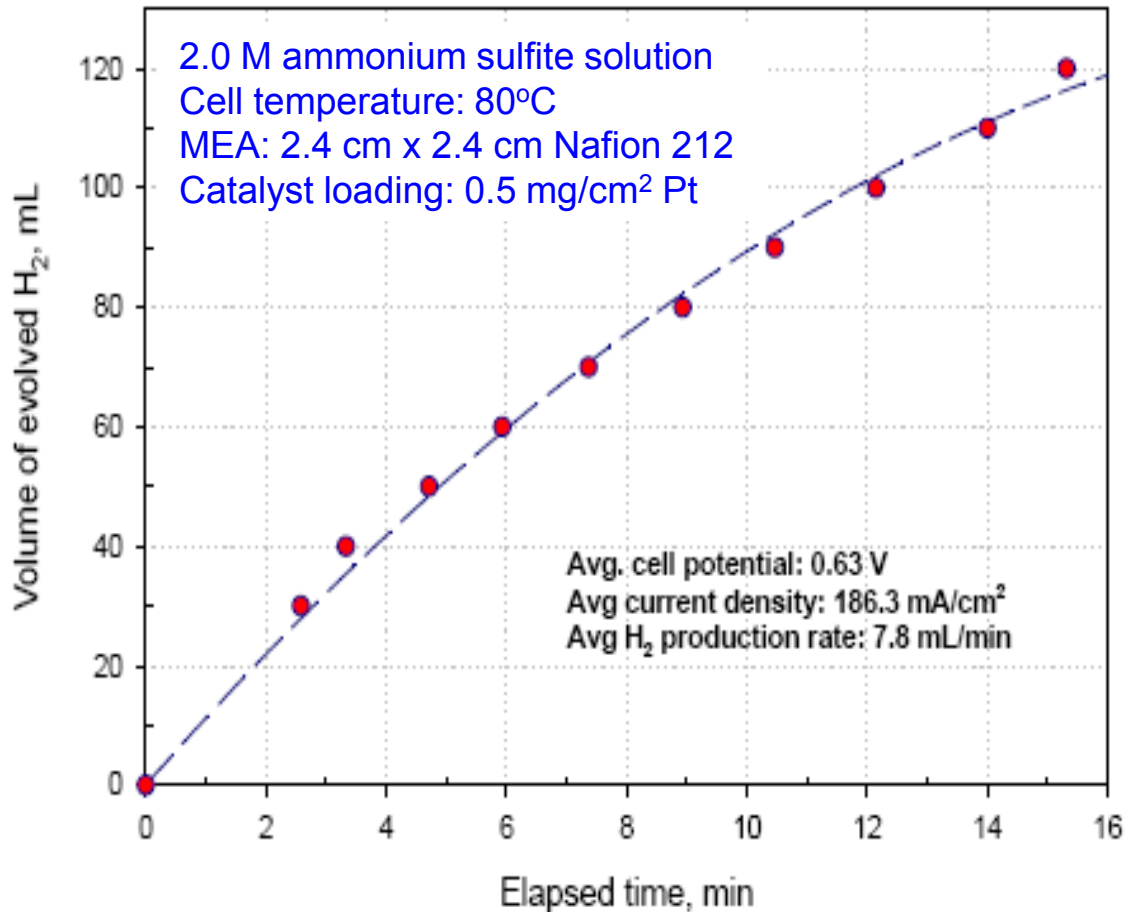
- Quantitative hydrogen production has been measured
- Voltage of electrolytic cell has been reduced from 1.2V to less than 1.0V by increasing temperature/pressure, controlling pH, and improving cell design



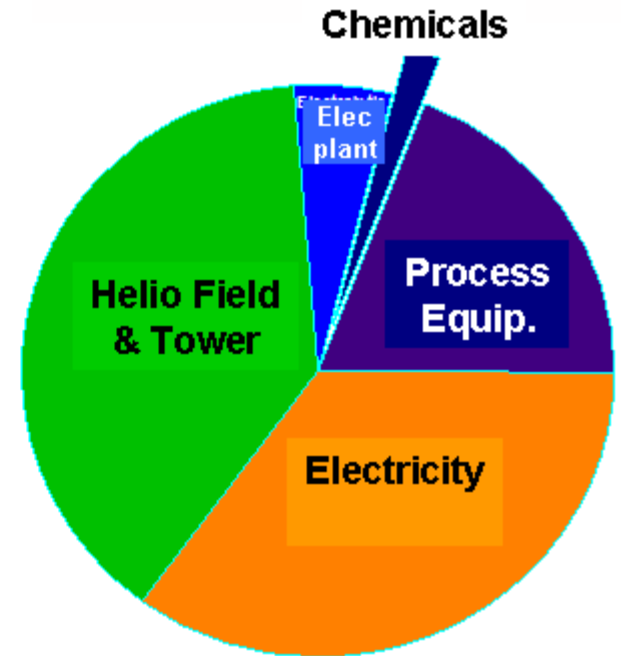
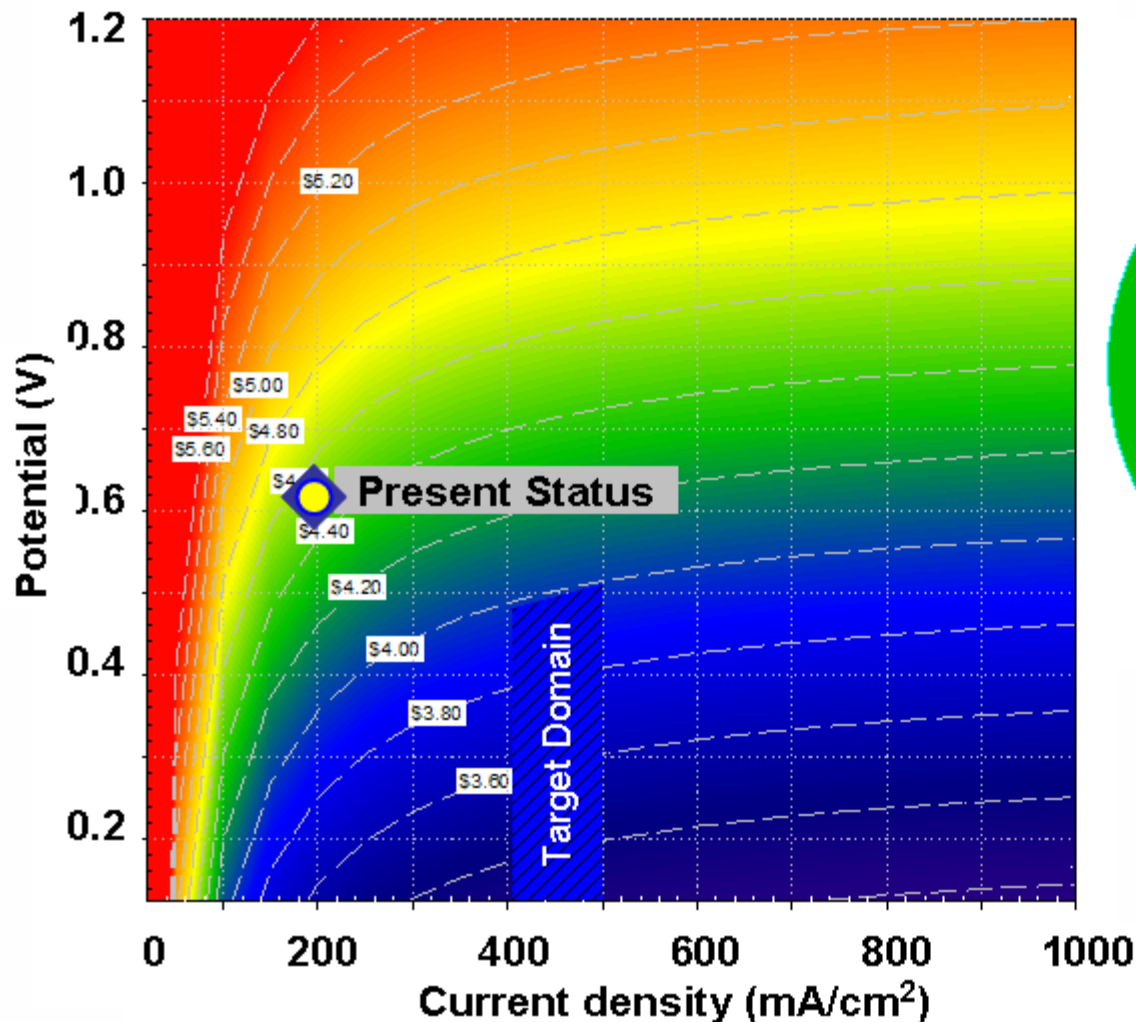
Target performance is:
Cell potential < 0.5V
cd > 400 mA/cm²

Electrolytic SA

FSEC has achieved 0.63 V at 186 mA/cm² using a proprietary new design/catalyst shown in the 16 min. test below

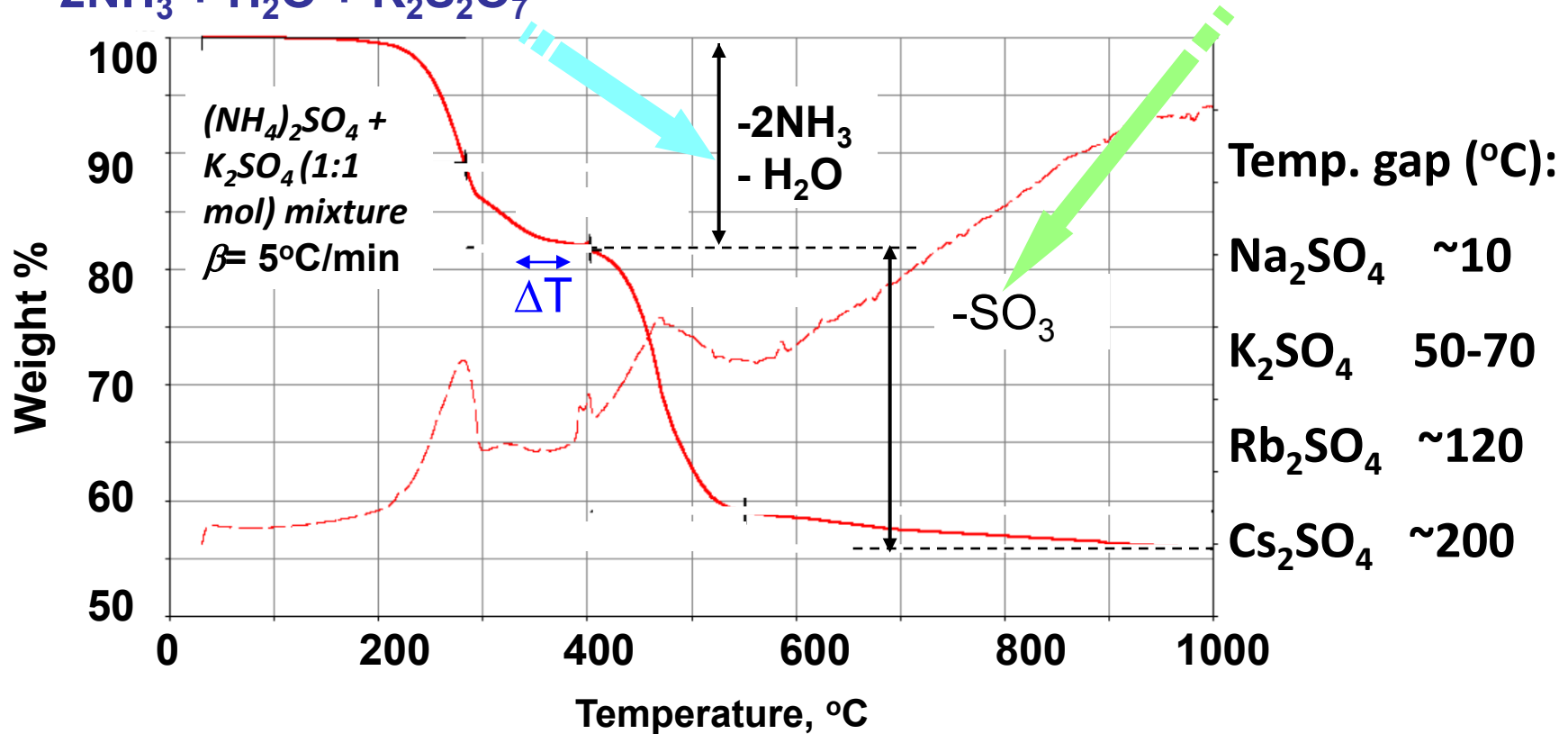
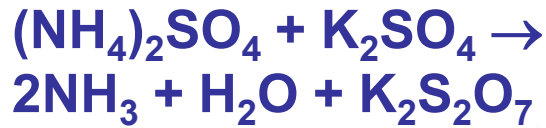


Present Status of Hybrid SA Cycle

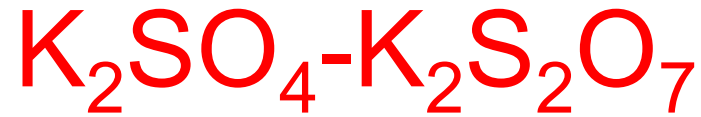


Key to meeting DOE H₂ production cost goals is reduction in the ammonium sulfite electro-oxidation overpotential

TG/DTG Analysis of $(\text{NH}_4)_2\text{SO}_4 - \text{K}_2\text{SO}_4$ Mixture



A large temperature gap is needed to separate NH₃ and SO₃ production stages



Sub-cycle – Remaining Issues

- ❖ Not sufficiently large temperature gap between NH_3 and SO_3 release stages. Possibility of cross contamination.
- ❖ Possibility of forming undesirable byproducts (e.g., NO).
- ❖ Low solubility of K_2SO_4 in molten $\text{K}_2\text{S}_2\text{O}_7$ (narrow window for molten state existence).

Hypothetical H₂A Analysis

H₂ cost vs. total capital & net utility costs

