

# Solar High-Temperature Water Splitting Cycle with Quantum Boost

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**PD\_09\_TRaissi**

# Overview

## Timeline

- **Start date: SEP 2007**
- **End date: APR 2012**
- **Percent complete: 25%**

## Budget

- **Total project funding**
  - DOE share: \$4M
  - Contractor share: \$1M
- **Funding for FY08: \$1.4M**
- **Funding for FY09: \$-0-**

## Barriers

- U. High-Temperature Thermochemical Technology
- V. High-Temperature Robust Materials
- W. Concentrated Solar Energy Capital Cost
- X. Coupling Concentrated Solar Energy & Thermochemical Cycles
- H<sub>2</sub> Production Target: **\$3.00/kg**
- Cycle Efficiency Target: **25%**

## Partners

- **SAIC (Lead)**  
Solar System/Receiver
- **UCF-FSEC**  
Process, Reactor/Receiver
- **Electrosynthesis**  
Salt electrolysis



# Objectives – Relevance (1)

- The focus of this project is to RD&D the viability of a new & improved sulfur family thermochemical water-splitting cycle (*i.e.* sulfur-ammonia cycle, SA) for large-scale hydrogen production using solar energy
- More specifically, our goal is to
  - Evaluate SA water splitting cycle that employs a photocatalytic scheme by which the visible portion of the solar spectrum is utilized for the production of hydrogen
  - Evaluate impact of H<sub>2</sub> production via electrolytic instead of photocatalytic scheme on the performance of the SA cycle
  - Perform economic analyses of the SA based cycles as they evolve
  - Select a cycle that has high potential for meeting the DOE's cost target of **\$3.00/kg hydrogen** generated & efficiency of 25%
  - Demonstrate technical feasibility of the selected SA cycle, in closed loop, at bench-scale
  - Demonstrate pre-commercial feasibility by testing & evaluation of a fully-integrated, pilot-scale closed cycle solar H<sub>2</sub> production plant

# Objectives – Relevance (2)

- **RY'09 activities involved:**
  - Completion of the Phase 1 sub-cycle testing & evaluation work with the goal of finalizing the overall configuration of the SA cycle that provides the best opportunity to meet DOE's hydrogen production cost & performance targets – Go-No Go decision to occur in Sept. 2009
  - Continuous development & optimization of the SA cycle's sub-processes
  - Detailed cost analysis (using the H2A platform) of all SA cycle configurations considered in order to identify where further improvements to the cycle could be made

# **RY '09 (Phase 1) Plan & Approach**

- **Sub-cycle Testing & Evaluation**

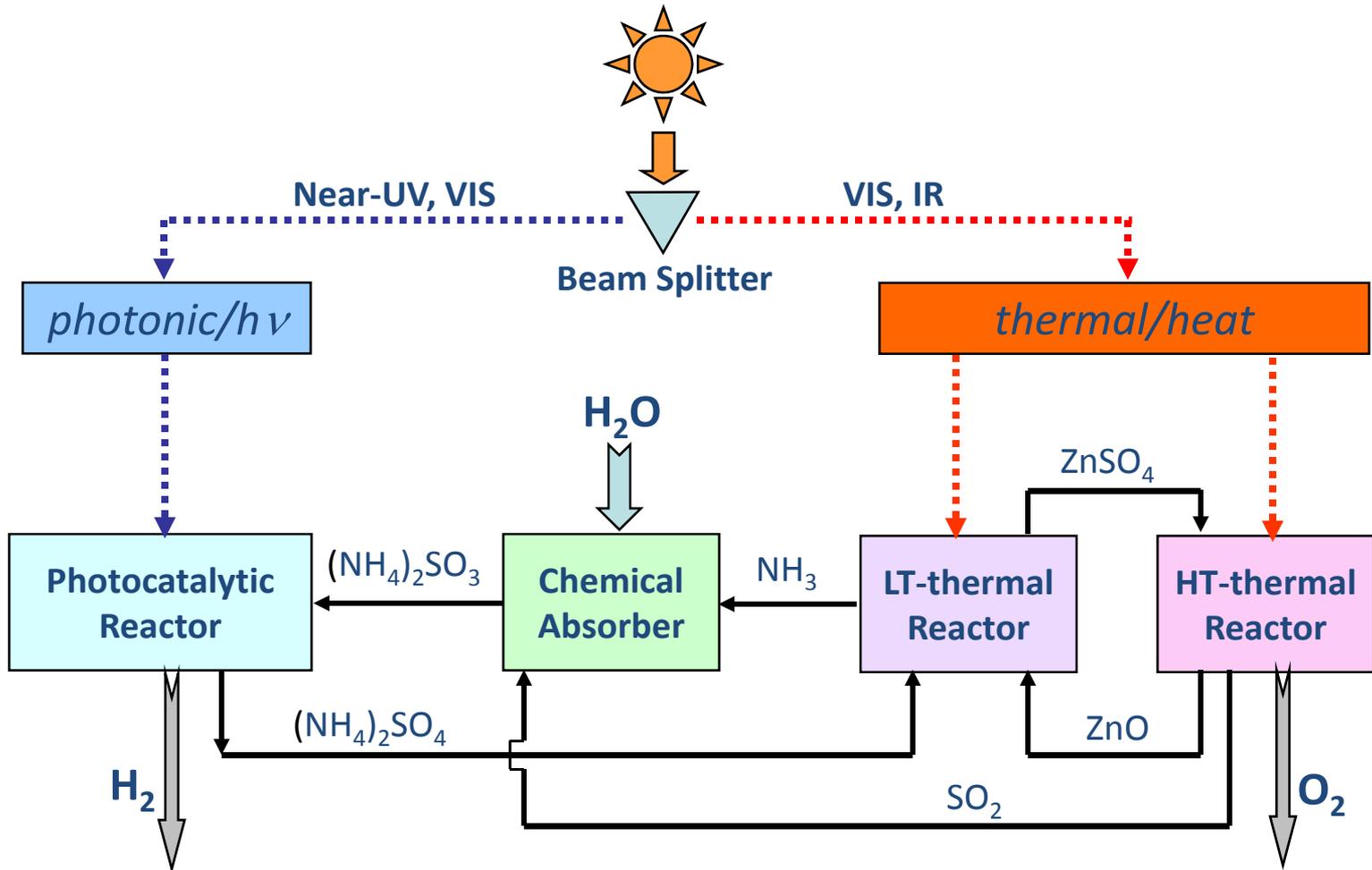
- Analysis of the SA thermochemical cycle with photocatalytic H<sub>2</sub> production scheme
- Analysis of the SA thermochemical cycle with electrolytic H<sub>2</sub> production scheme
- Lab evaluation of the selected cycle(s) & processes
- Reactor/receiver configuration

- **Solar Concentrator Design**

- Concentrator specifications
- Preliminary concentrator design
- Subsystem testing

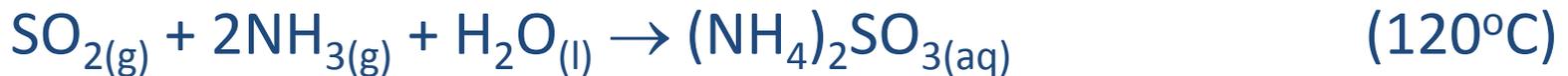
- **H2A Cost Analysis**

# Photocatalytic SA Cycle (1)



See Supp. Slide 45

# Photocatalytic SA Cycle Reactions



# Accomplishments (1)

## Photocatalytic-SA Cycle

- Cycle has been closed (Aspen™ flowsheet)
- All reaction steps have been experimentally validated
- No side reactions occurred
- All chemicals & reagents used in the cycle are readily available
- All materials of construction & component challenges have been addressed
- Overall efficiency of the dual-field photocatalytic SA cycle is not likely to meet the DOE target of 25%
- Hydrogen production cost for the photocatalytic SA cycle with split beam arrangement is not likely to meet the DOE target of \$3.00/kg

# Accomplishments (2)

## Photocatalytic-SA Cycle

- **Demonstrated successes**

- Photocatalyst optimization improved the photon-to-H<sub>2</sub> energy conversion efficiency from less than 12% (year & half ago) to more than 28% (recently) using CdS doped with multi-metal co-catalysts
- Stability of the photocatalyst has been demonstrated over many days of continuous operation
- Non-Pt dopants have been identified having close to 20% photon-to-H<sub>2</sub> energy conversion efficiency
- The chemistry of ZnO sub-cycle for oxygen evolution has been thoroughly investigated & shown to be “clean”, with no undesirable side reactions occurring
- Ammonium sulfate reacts with ZnO forming ZnSO<sub>4</sub>, ammonia & water vapor at temperatures below 500°C
- Complete decomposition of zinc sulfate occurs at temperatures as low as 900°C, producing ZnO, oxygen and SO<sub>2</sub> gas

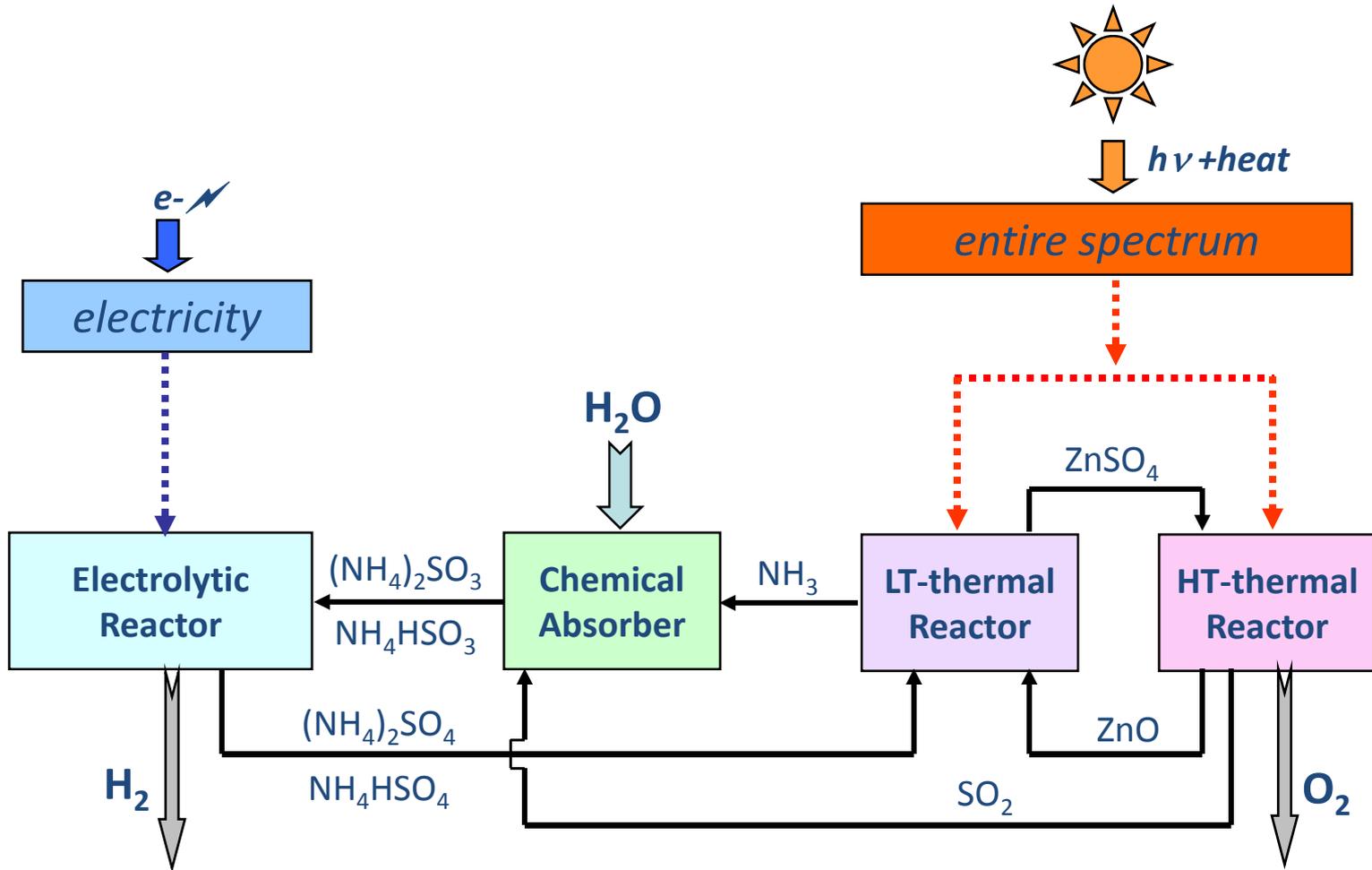
# Photocatalytic SA Cycle Strengths

- **Solar cycle:** Employs photonic and thermal components of the solar resource. Does not need electric power to operate hydrogen production process
- **Simple separations:** There are no complex gas and/or liquid separation stages involved
- **Simple photoreactor design:** The photo-catalytic reactor operates at near ambient conditions & can be made from low-cost materials

# Photocatalytic SA Cycle Weaknesses

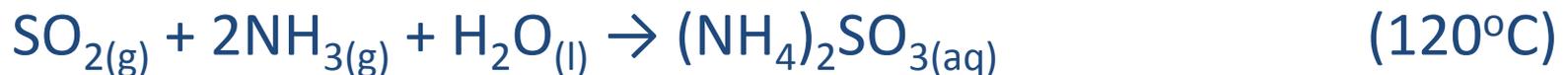
- **Employs noble metals:** Pt makes up 70 wt% of dopants & close to 60 wt% of total cost of chemicals & reagents used in the cycle
- **Large photoreactor footprint:** If dual field configuration is used
- **Spectral beam-splitting:** Splitting solar spectrum allows higher cycle efficiency at the cost of complexity and a larger heliostat field. Separation of the photoreactor and thermal solar fields yields lower solar efficiency but potentially lower hydrogen production cost due to increased land use

# Electrolytic SA Cycle



# Electrolytic SA Cycle Reactions

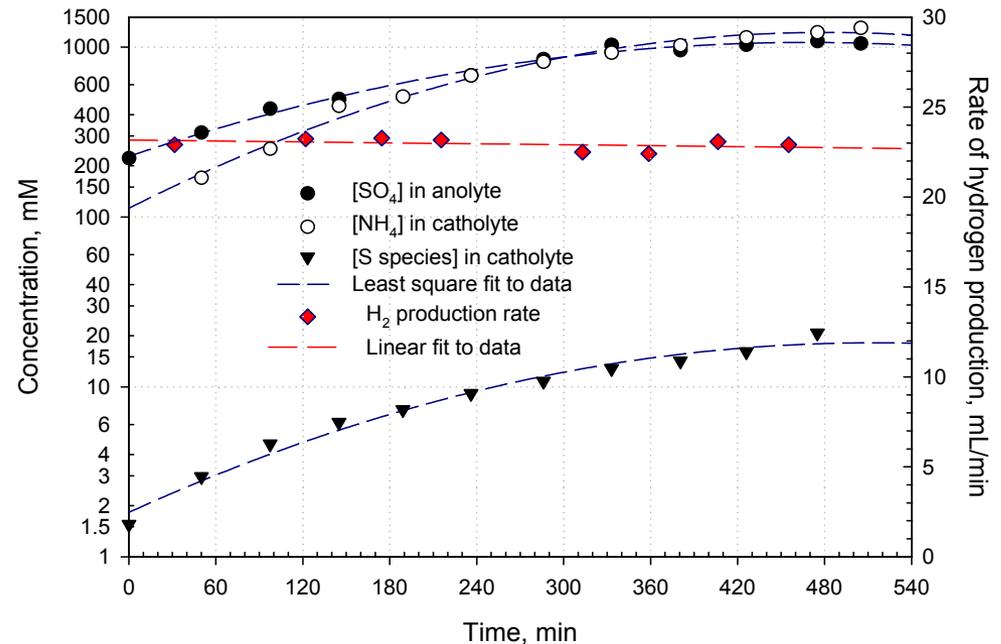
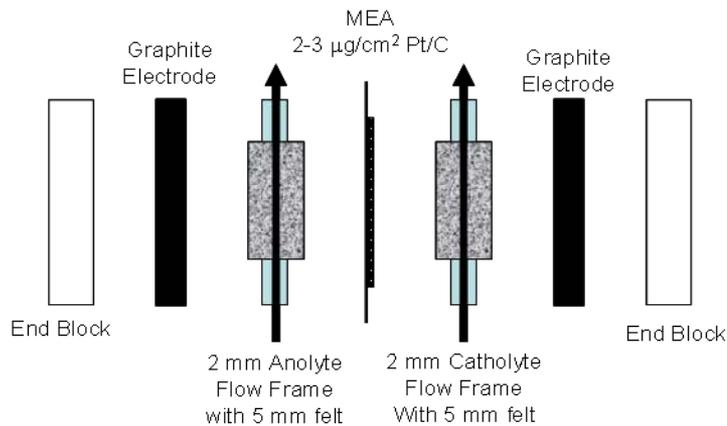
In the electrolyzer operating at ~50-60°C:



# Electro-Oxidation of Ammonium Sulfite

## Single Cell Results (1)

GFD anode, NRE111 MEA cathode ( $\sim 2\mu\text{g Pt}/\text{cm}^2$ )

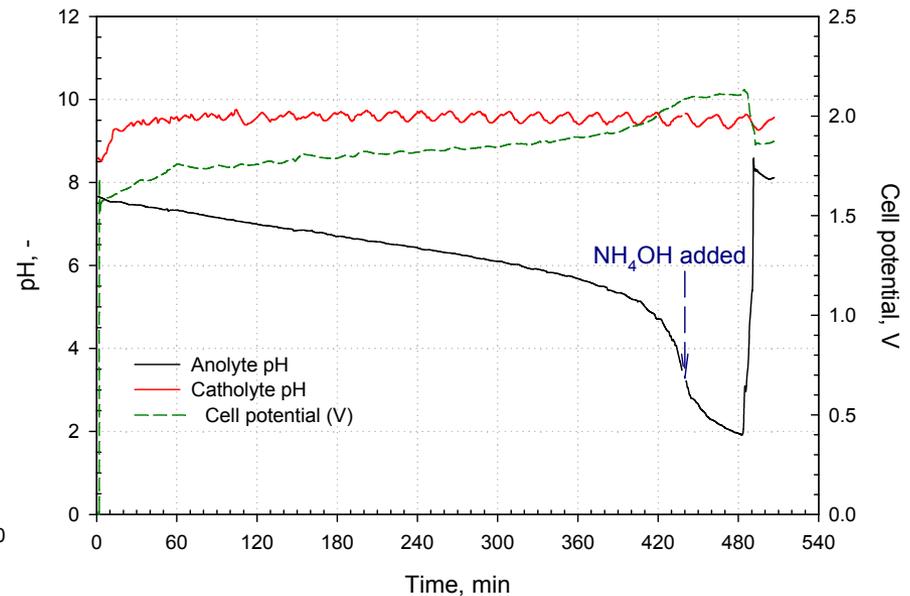
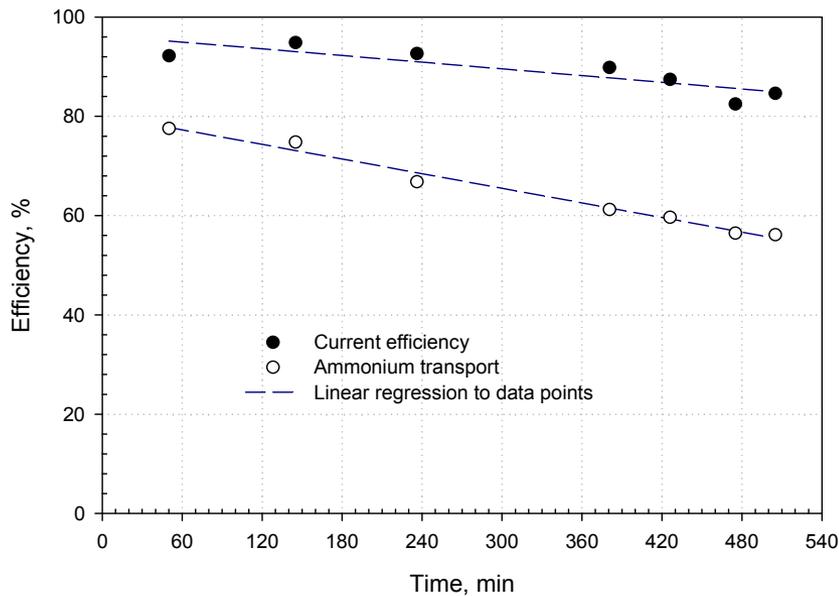


➤ Quantitative hydrogen evolution & sulfite oxidation

# Electro-Oxidation of Ammonium Sulfite

## Single Cell Results (2)

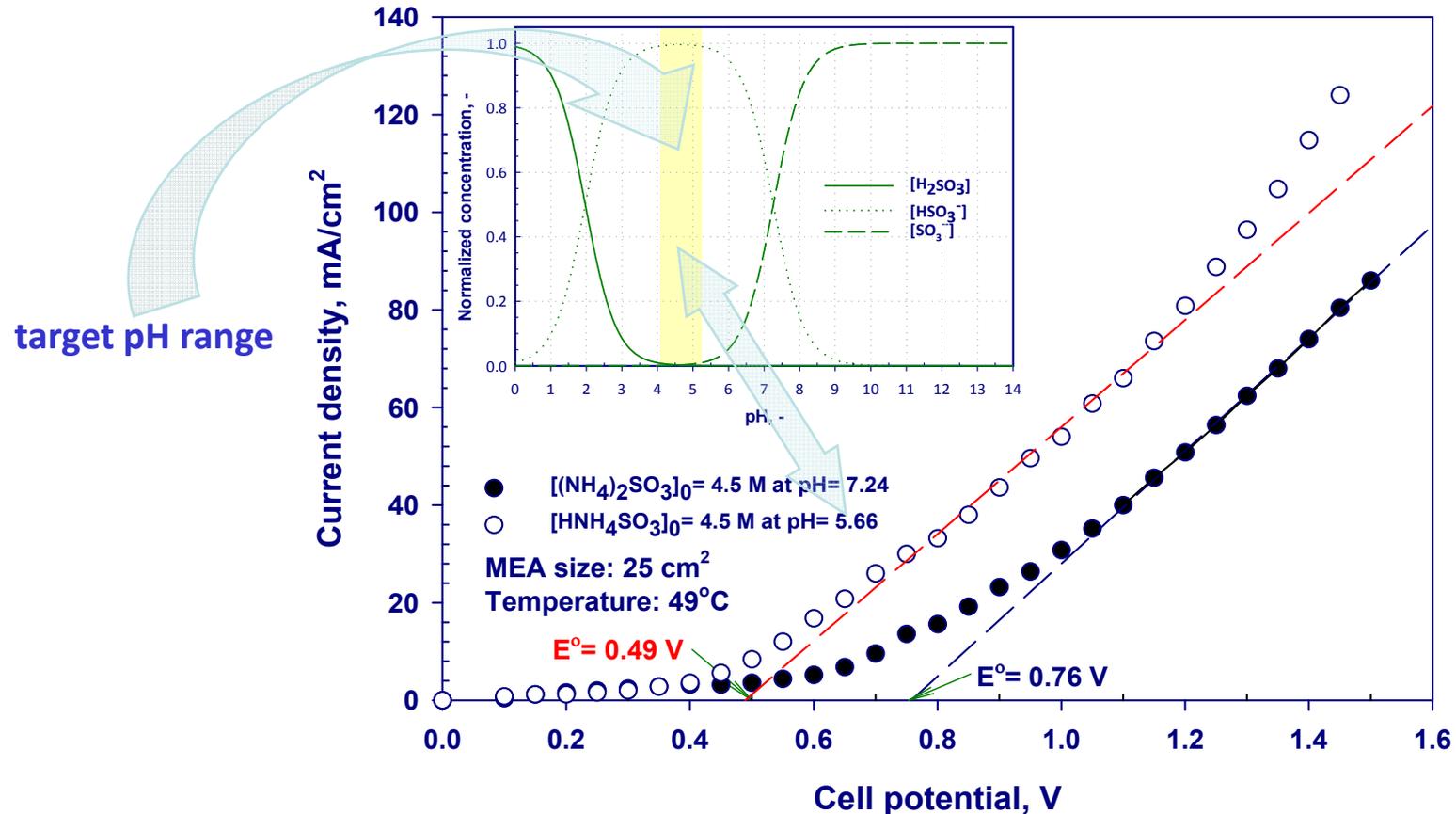
GFD anode, NRE111 MEA cathode ( $\sim 2\mu\text{g Pt}/\text{cm}^2$ )



➤ Transport number for ammonium ion across membrane  $\approx 0.6$

➤ Cell Voltage is pH dependent

# Electro-Oxidation of Ammonium Bisulfite



➤ Open circuit voltage of bisulfite oxidation in acidic media is less than that of sulfite

# Electrolytic SA Cycle

## Strengths & Weaknesses

- **Strengths**

- Small footprint
- High current efficiency
- Potentially lower capital cost than photocatalytic hydrogen production
- 24-7 operation possible

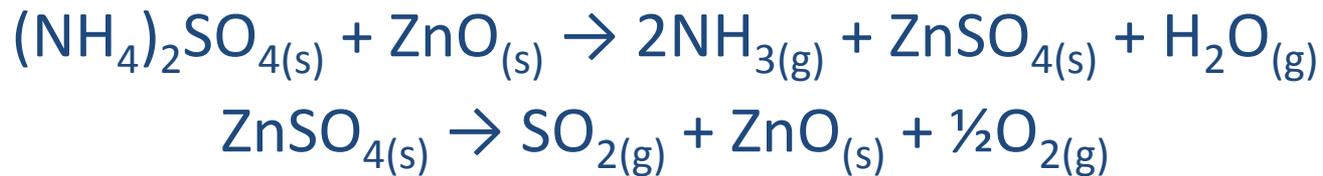
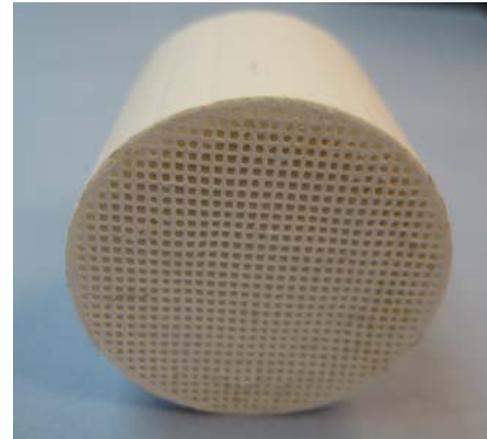
- **Weaknesses**

- May require noble metal electrodes
- Low current densities at low cell overpotentials
- 24-7 operation requires high temperature TES to keep the oxygen production sub-cycle running

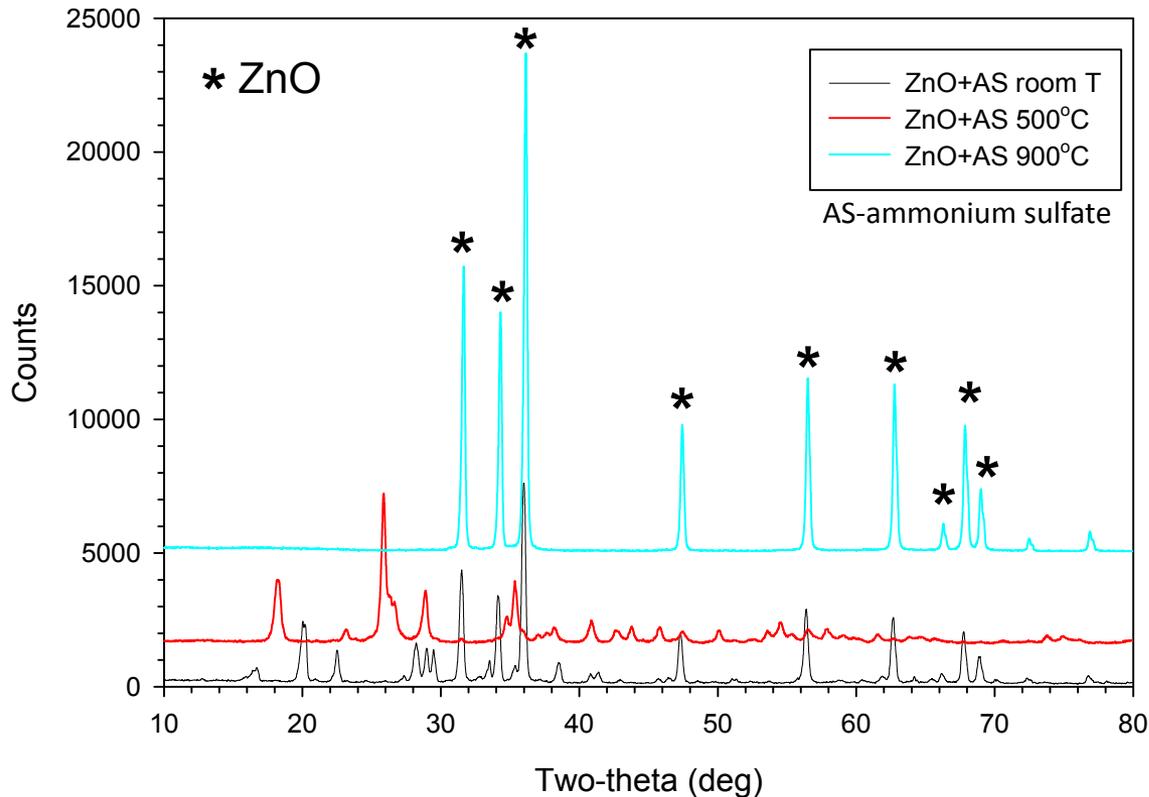
# Oxygen Production Sub-Cycle



Alundum-supported zinc oxide

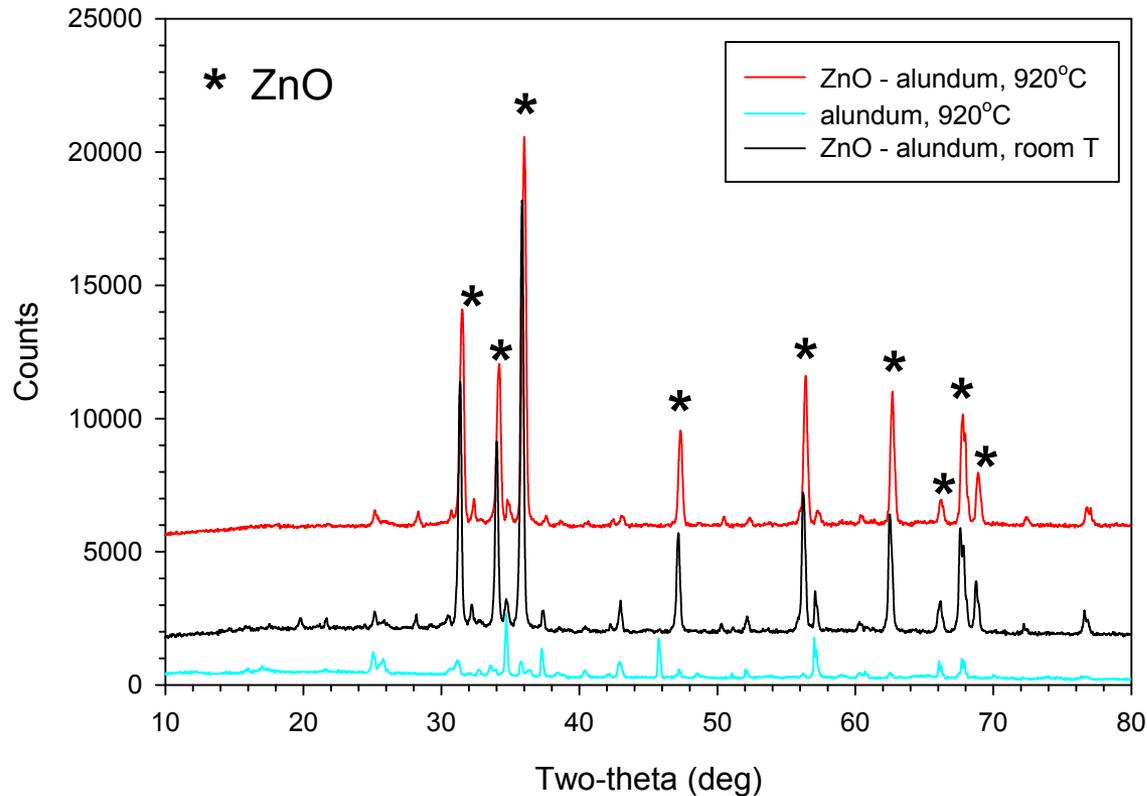


# XRD of ZnO-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (1:1 mol) Mix Reacted at 500° & 900°C



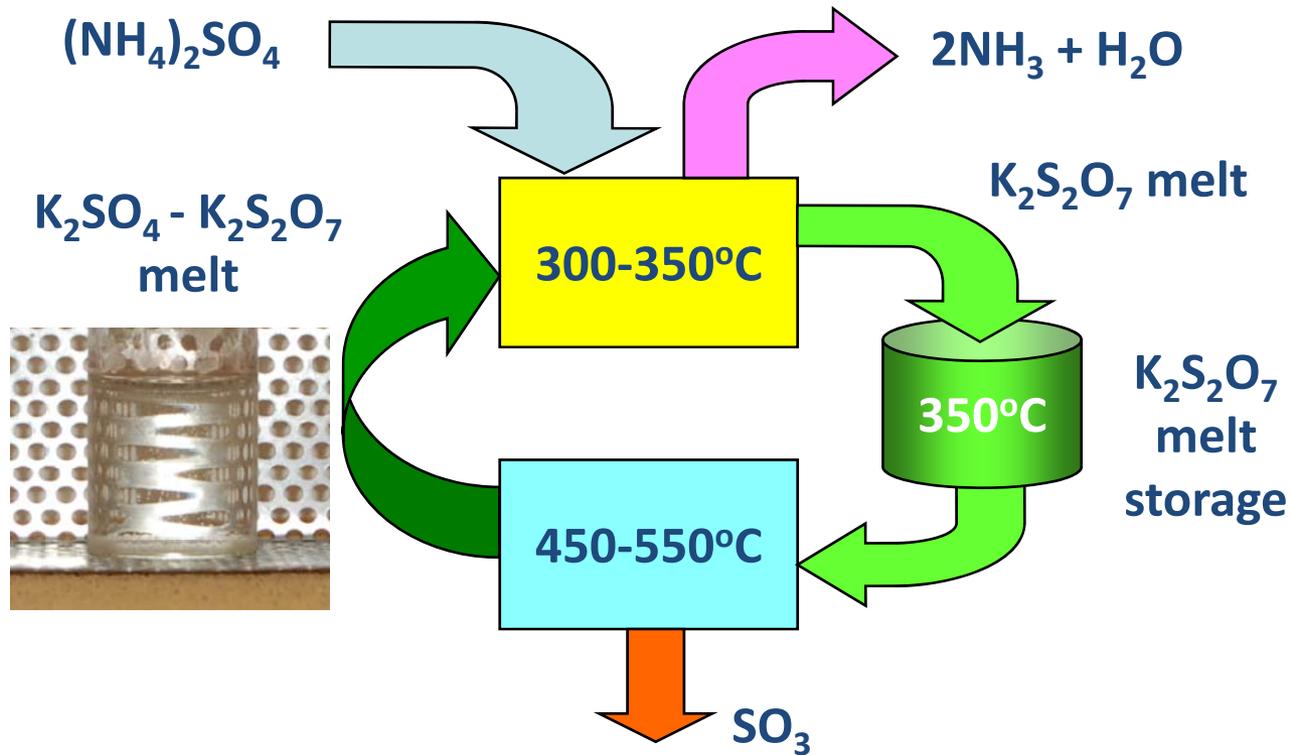
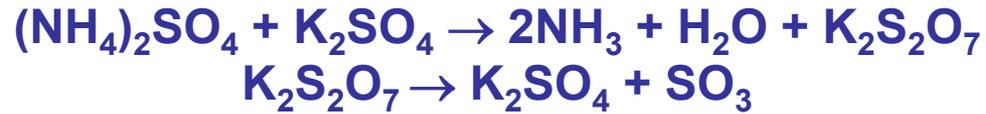
**ZnO reacts with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at 500°C forming ZnSO<sub>4</sub>, & ZnO is completely regenerated at 900°C**

# XRD of ZnO- Alundum Mix



**ZnO does not react with alundum support  
at temperatures up to 920°C**

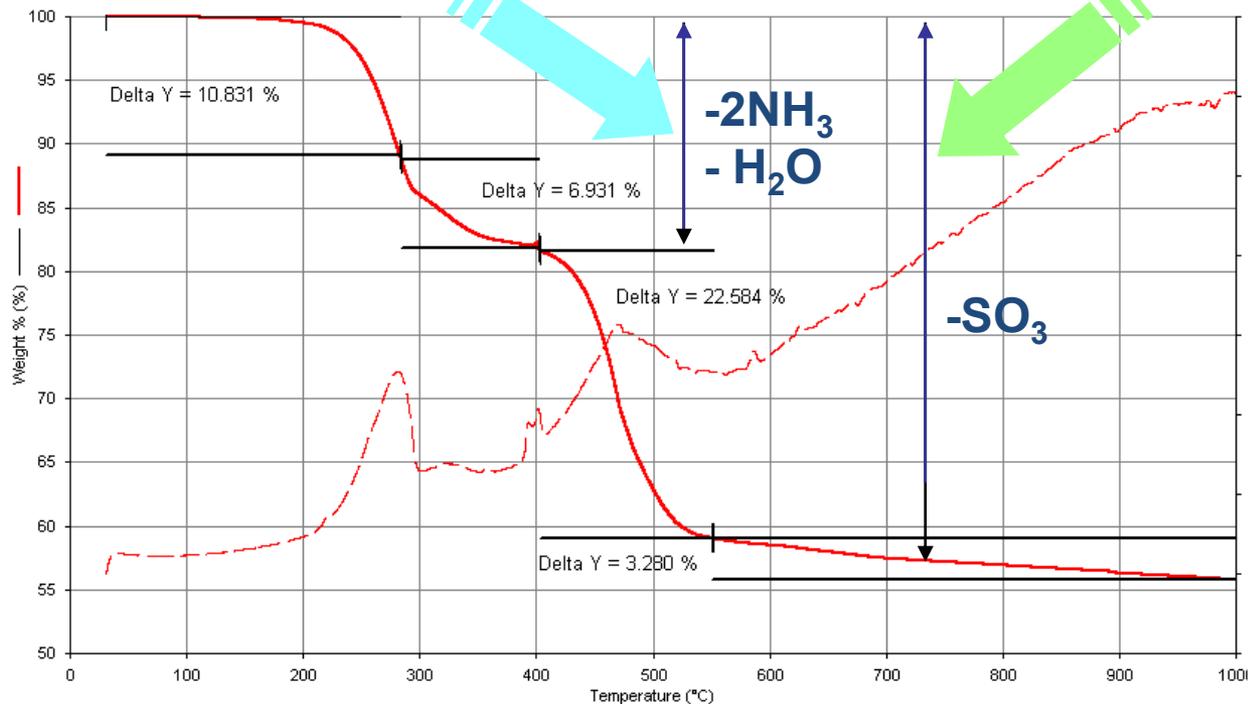
# $K_2SO_4$ Sub-Cycle for $O_2$ Production (1)



$K_2SO_4$  sub-cycle allows transportation & high-temperature storage of the intermediate salts in liquid (melt) form

# $K_2SO_4$ Sub-Cycle for $O_2$ Production (2)

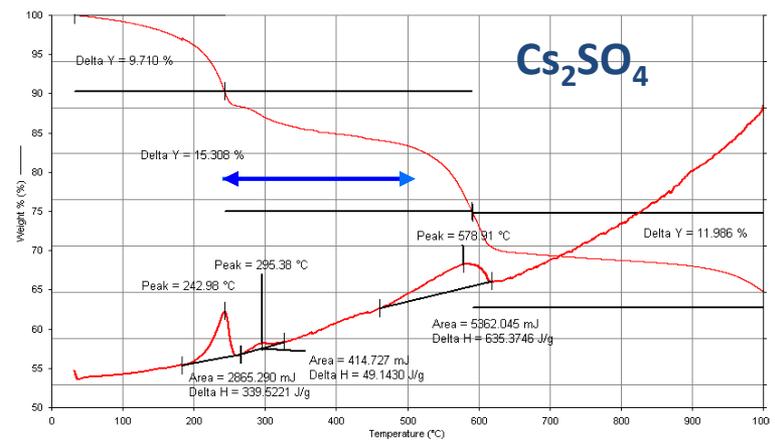
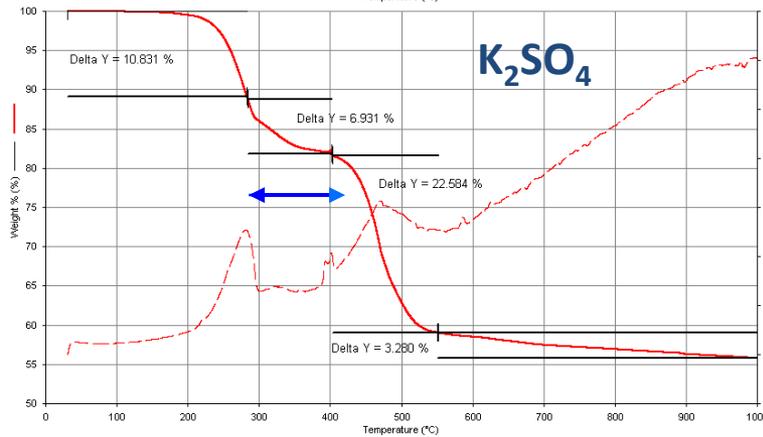
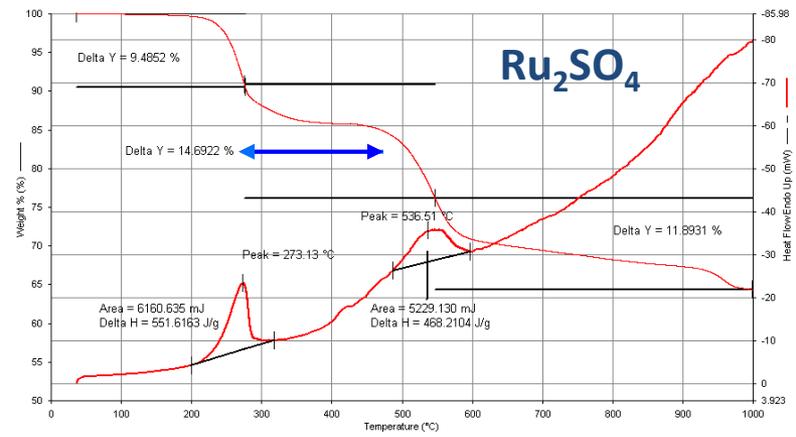
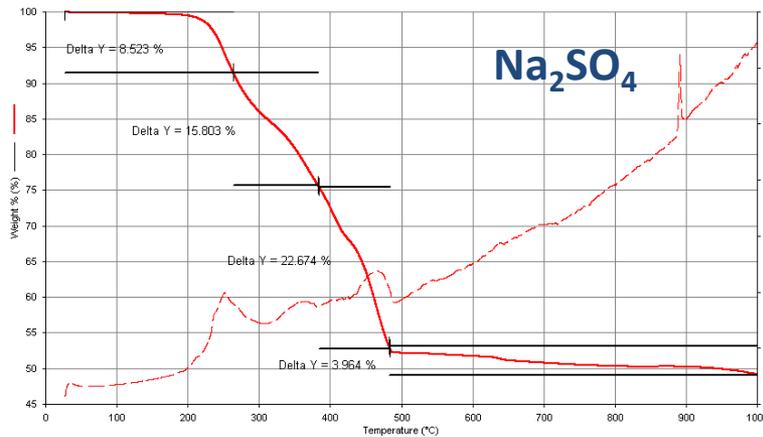
*TG/DTA of  $(NH_4)_2SO_4 + K_2SO_4$  (1:1 mol) mixture at  $5^\circ C/min$*



**A broad temperature plateau of about  $150^\circ C$  allows straightforward  $NH_3$  &  $SO_3$  separation**

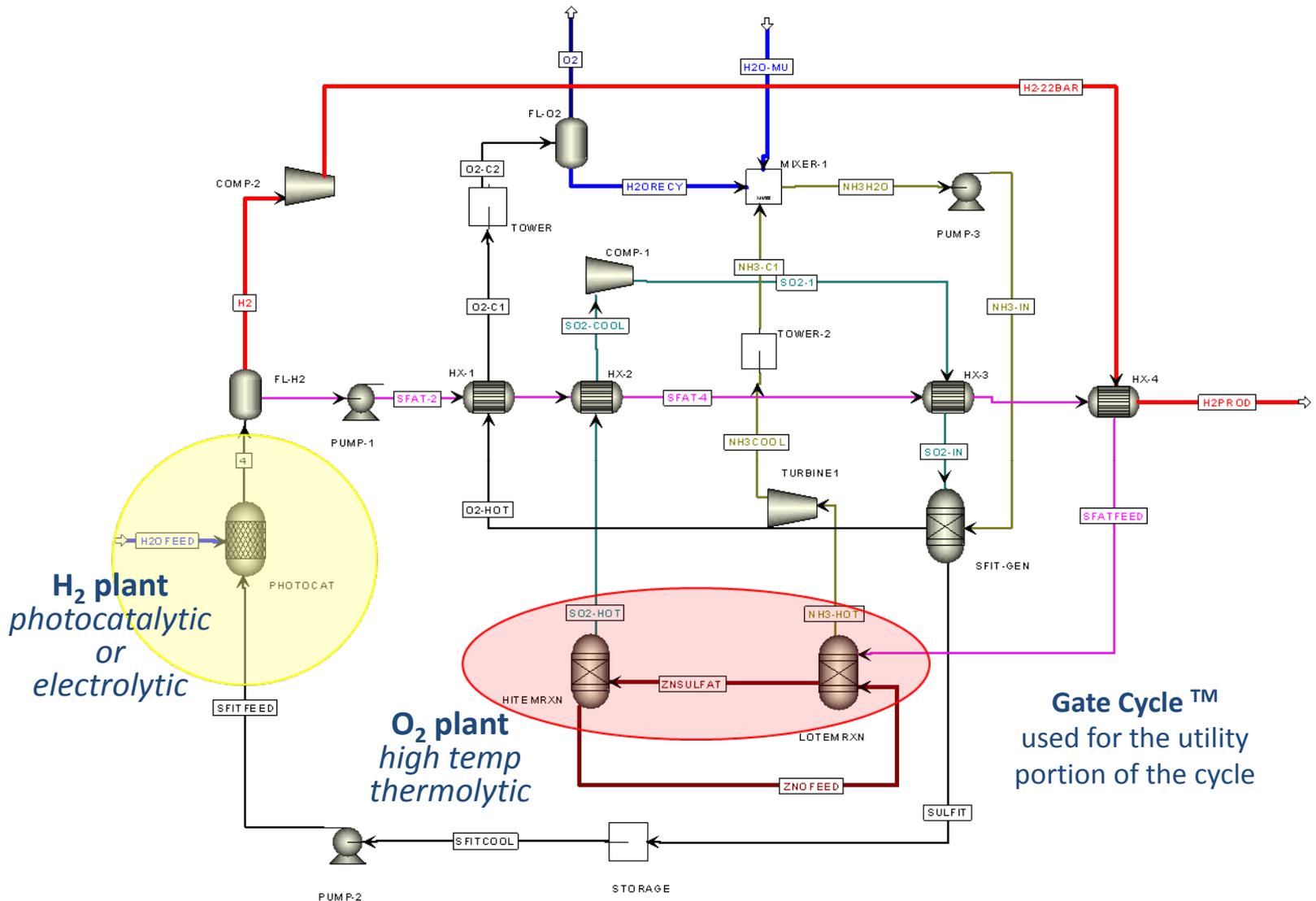
# K<sub>2</sub>SO<sub>4</sub> Sub-Cycle for O<sub>2</sub> Production (3)

TG/DTA of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>: M<sub>2</sub>SO<sub>4</sub> = 1:1 (mol) mixture, M = Na, K, Ru, Cs



**K<sub>2</sub>SO<sub>4</sub> is the least costly with the broadest temperature plateau of all alkali metal sulfates tested for facile separation of NH<sub>3</sub> & SO<sub>3</sub>**

# Aspen™ Flowsheet of SA Cycle



# Approach

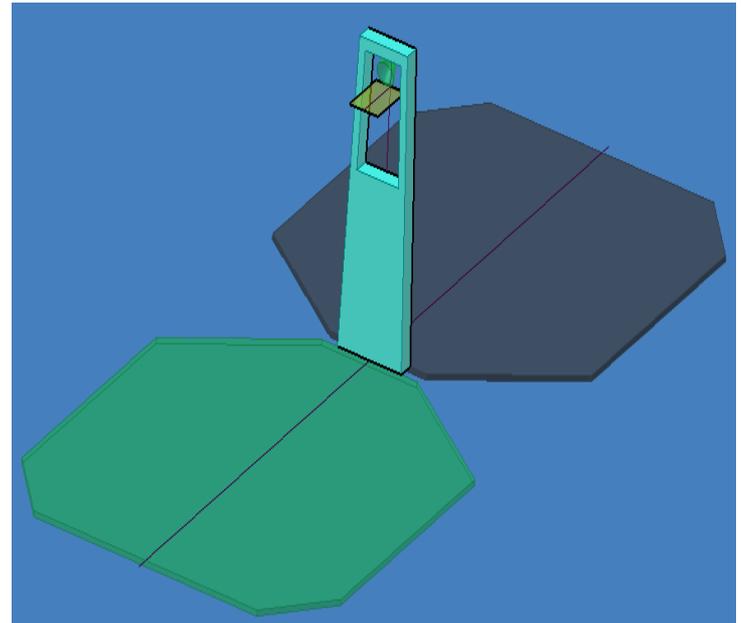
## Solar Interface Issues

- Configure solar field optimally for integration with thermochemical plant
- Develop low-cost heliostat to reduce capital cost of solar field (this benefits any heliostat-based system – solar power, hydrogen, ....)

# Technical Progress (1)

- **Photoreactor System Evaluation**

- Best beam-splitting configuration determined to be North-field heliostat field with cold mirror near focus & South-field photoreactors operating at  $\sim 2$  suns



- Most cost-effective approach overall is central receiver system for thermal loads & separate one-sun photoreactor field

# Technical Progress (2)

- **Central receiver system and receivers optimized to deliver energy to low-temp and high-temp reactors of S-A process**
  - 125 m tower, 68,800 m<sup>2</sup> of North-field heliostats
  - 2/3 – 1/3 split in power between reactors; Temperatures of 500°C and 800°C
  - 6 m<sup>2</sup> aperture high-temp receiver, 700 suns max
  - 8.5 m<sup>2</sup> aperture low-temp receiver, 900 suns max
  - Heliostat aim points moved between receivers to balance power requirements in real time
  - 45-55 MW<sub>th</sub> peak power, approx. 140 GWh<sub>th</sub> annually delivered to chemical reactors

# Technical Progress (3)

- **Demonstrated low-cost glass-reinforced concrete (GRC) heliostat system**
  - Half-scale prototype completed & undergoing tests
  - Demonstrated viability of fabrication approaches
  - Demonstrated drive system features & controls
  - Installed system cost projected  $< \$100/\text{m}^2$



# H2A Analysis

## Photocatalytic SA Cycle

- H2A analysis has been completed
- Preliminary value with TIAX comments incorporated is **\$5.31/kg (2015)**.
  - Added staffing, replacement costs, 3-year construction time, taxes, chemical equipment installed costs, \$126.50 heliostats, indirect costs, maintenance & repair costs

# H2A Results

## Photocatalytic SA Cycle

| <i>Specific Item Cost Calculation</i>                 |                                  |                              |
|---|----------------------------------|------------------------------|
| <b>Cost Component</b>                                 | <b>Cost Contribution (\$/kg)</b> | <b>Percentage of H2 Cost</b> |
| <b>Capital Costs</b>                                  | <b>\$5.09</b>                    | <b>96.0%</b>                 |
| <b>Decommissioning Costs</b>                          | <b>\$0.01</b>                    | <b>0.2%</b>                  |
| <b>Fixed O&amp;M</b>                                  | <b>\$1.69</b>                    | <b>31.8%</b>                 |
| <b>Feedstock Costs</b>                                | <b>\$0.00</b>                    | <b>0.0%</b>                  |
| <b>Other Raw Material Costs</b>                       | <b>\$0.00</b>                    | <b>0.0%</b>                  |
| <b>Byproduct Credits</b>                              | <b>-\$1.50</b>                   | <b>-28.2%</b>                |
| <b>Other Variable Costs<br/>(including utilities)</b> | <b>\$0.01</b>                    | <b>0.3%</b>                  |
| <b>Total</b>  | <b>\$5.31</b>                    |                              |

# Collaborations

- **Partners**

- **Science Applications International Corp. (Industry)**

- Contract management & LEAD
    - Solar concentrator/receiver development & system integration
    - Pilot & full-scale system design & costing

- **UCF/Florida Solar Energy Center (Academic partner)**

- Cycle & process development, evaluation & selection
    - Reactor/receiver & system level design & optimization

- **Electrosynthesis Company, Inc. (Industry & sub)**

- Salt electrolysis
    - Electrolytic cell design & optimization

# Electro-oxidation of Ammonium Sulfite – Future Work

- Anodic oxidation of sulfite & the cathodic hydrogen evolution reaction are pH dependent
  - $\text{SO}_4^{2-} + 4 \text{H}^+ + 2 \text{e}^- \leftrightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$       $E^0 = +0.172 \text{ V/nhe}$
  - $\text{SO}_4^{2-} + \text{H}_2\text{O} + 2 \text{e}^- \leftrightarrow \text{SO}_3^{2-} + 2\text{OH}^-$       $E^0 = -0.930 \text{ V/nhe}$
- Main source of voltage loss is due to the anode losses
  - Target cell voltage <1V
  - Find conditions where anode can be run at high pH without adverse effect on localized pH changes
    - **Introduce some buffering capacity into the solution**
    - **Explore the use of anion exchange membranes as the basis for the MEA**
    - **Explore the use of undivided cells**
    - **Need to maintain pH conditions where the sulfite will not be further reduced**
  - Find catalysts that will reduce the over-potential at the anode and allow operation at high current densities
  - Examine molten salts
- Recombine anolyte & catholyte streams to maintain fixed pH

# Solar Interface – Future Work

- Refine solar field and receiver design as chemical plant needs evolve
- Detailed production cost estimate for GRC heliostat system based on prototype test results
- Full-scale prototype of pre-commercial GRC heliostat design

# SA Cycle – Future Work

- **Completion of phase 1 activities**
  - Document photocatalytic-SA cycle results
  - Complete electrolytic H<sub>2</sub> production tests
  - Finalize thermal reactor/receiver design
  - Finalize solar field configuration & design
  - Complete electrolytic H<sub>2</sub>A analysis

# Summary

- Photocatalytic-SA cycle is not likely to meet DOE's hydrogen production cost goals without a major effort to reduce the cost of hot mirrors to allow SB implementation
- Electrolytic SA cycle is in early development stage, so further performance improvements & cost reductions are likely
- Electrolytic-SA cycle has potential to meet DOE's hydrogen production and efficiency goals
- GRC has promise to reduce heliostat cost

**Questions?**

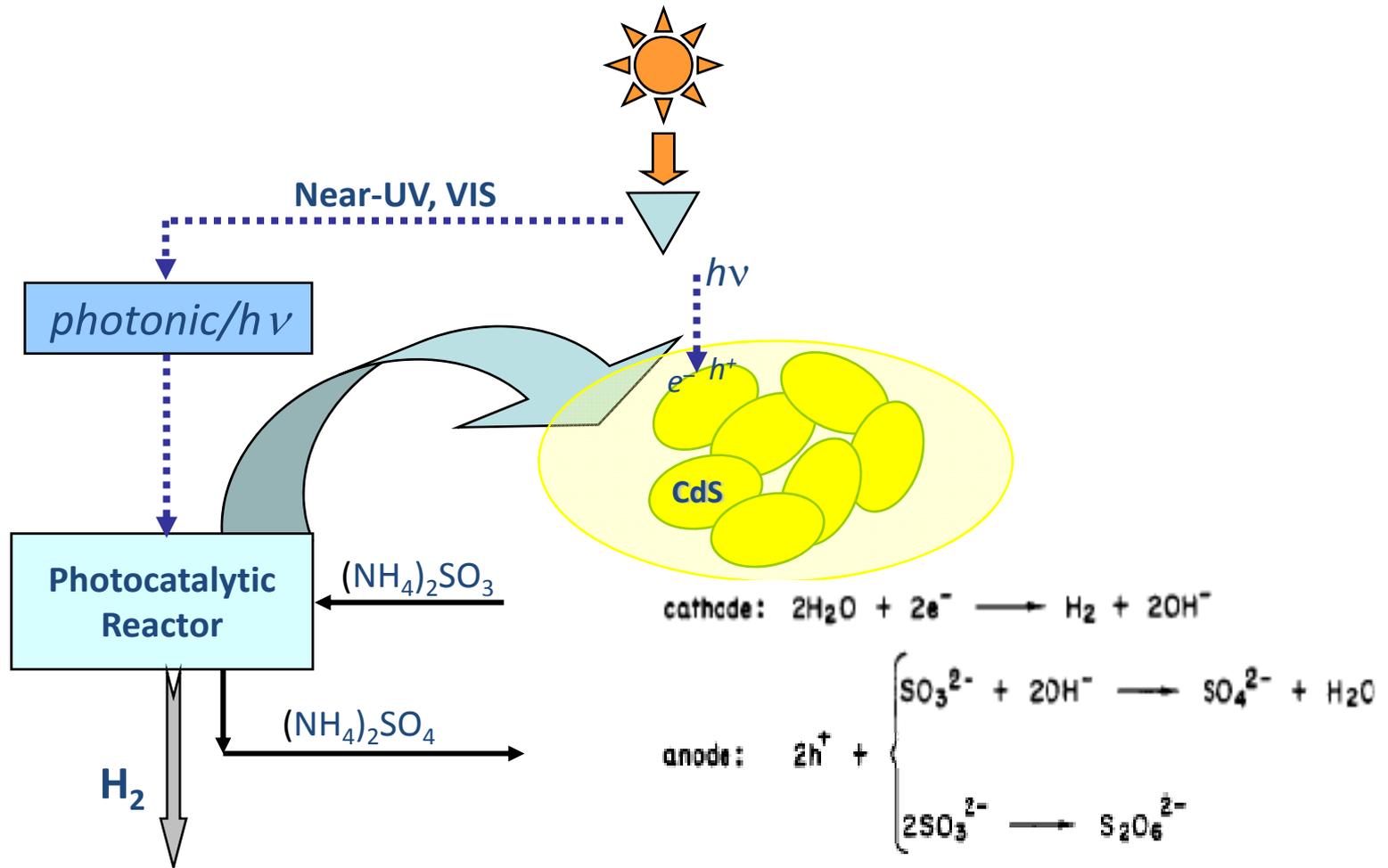
# Supplemental Slides

# Milestones, Schedule & Deliverables

| Month Year   | Type                         | Description/Requirements  | Status             |
|--------------|------------------------------|---|--------------------|
| Aug /Sep '09 | Activity                     | Develop & optimize the processes that make up the SA water-splitting cycle so that the cycle can meet the DOE cost & performance targets  | Nearing Completion |
|              |                              | Complete preliminary design of solar concentrator for pilot-scale system  |                    |
|              |                              | Incorporate know-how from sub-cycle work & those obtained from the H2A analysis into the design of the fully integrated bench scale system  | ongoing            |
| Sep '09      | <b>GO/ NO-GO To Phase 2*</b> | The SA cycle has been shown to meet DOE's cost & performance goals, and non-federal cost share is in place for Phase 2  |                    |
| Sep '10      | Activity                     | Build, test & operate the fully integrated closed loop bench-scale SA cycle   | Future Activities  |
| Sep '10      | <b>GO/ NO-GO To Phase 3#</b> | Bench-scale results for the fully integrated closed SA cycle is shown to be technologically feasible & able to meet DOE's hydrogen production cost & performance targets for 2010 (\$3/kg of H <sub>2</sub> or less) to support scaling-up to pilot-scale demonstration |                    |
| Mar '11      | Activity                     | Design or identify a suitable solar concentrator for the pilot-scale experiments. Begin the design of the pilot-scale receiver/reactor  |                    |
| Nov '11      |                              | Complete the hardware set up for the solar concentrator & receiver system   |                    |
| Apr '12      | Report                       | Complete testing of the full-scale system. Compile the data and prepare final report on the cost figures & recommendations for further development  |                    |

\* Bench-scale testing of the complete cycle & pilot plant design # Pilot-scale demonstration

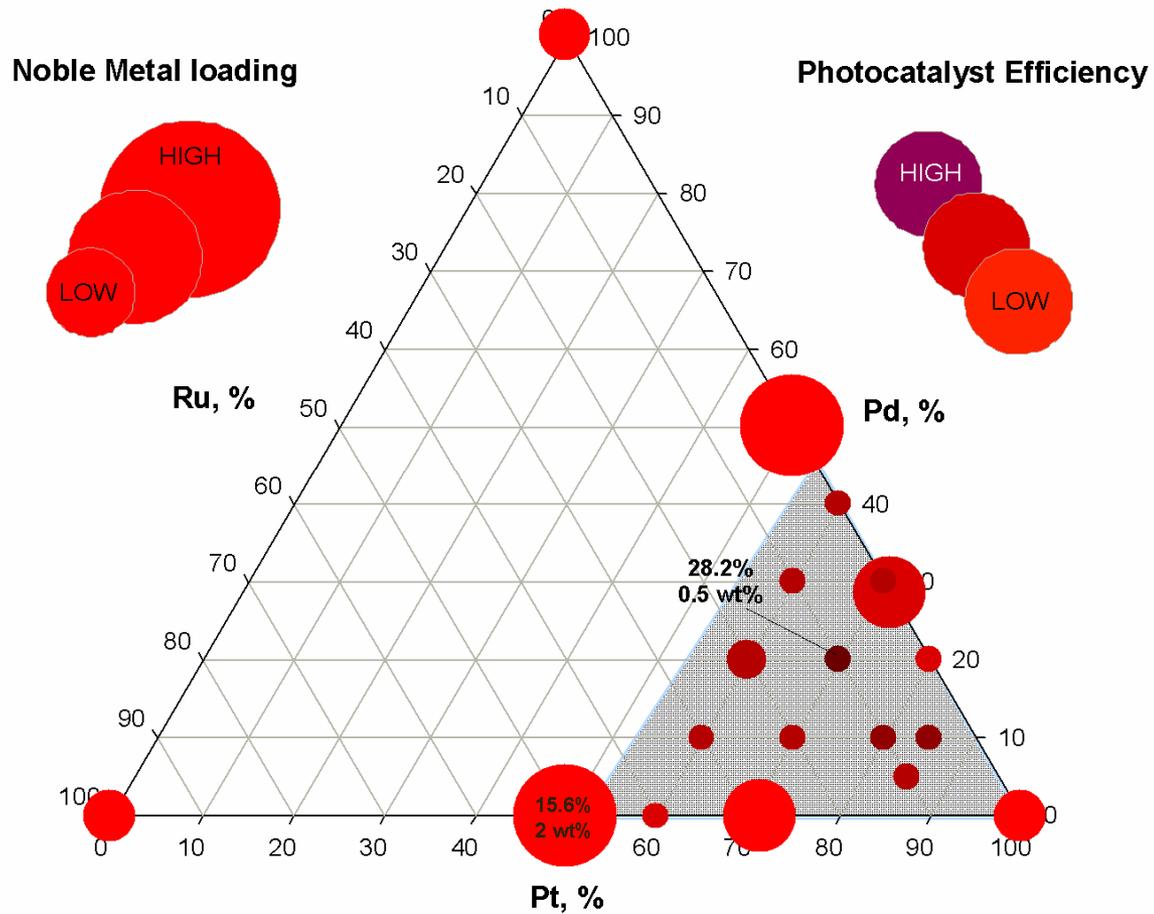
# Photocatalytic SA Cycle (2)



# Optimization of Hydrogen Production Photocatalysts



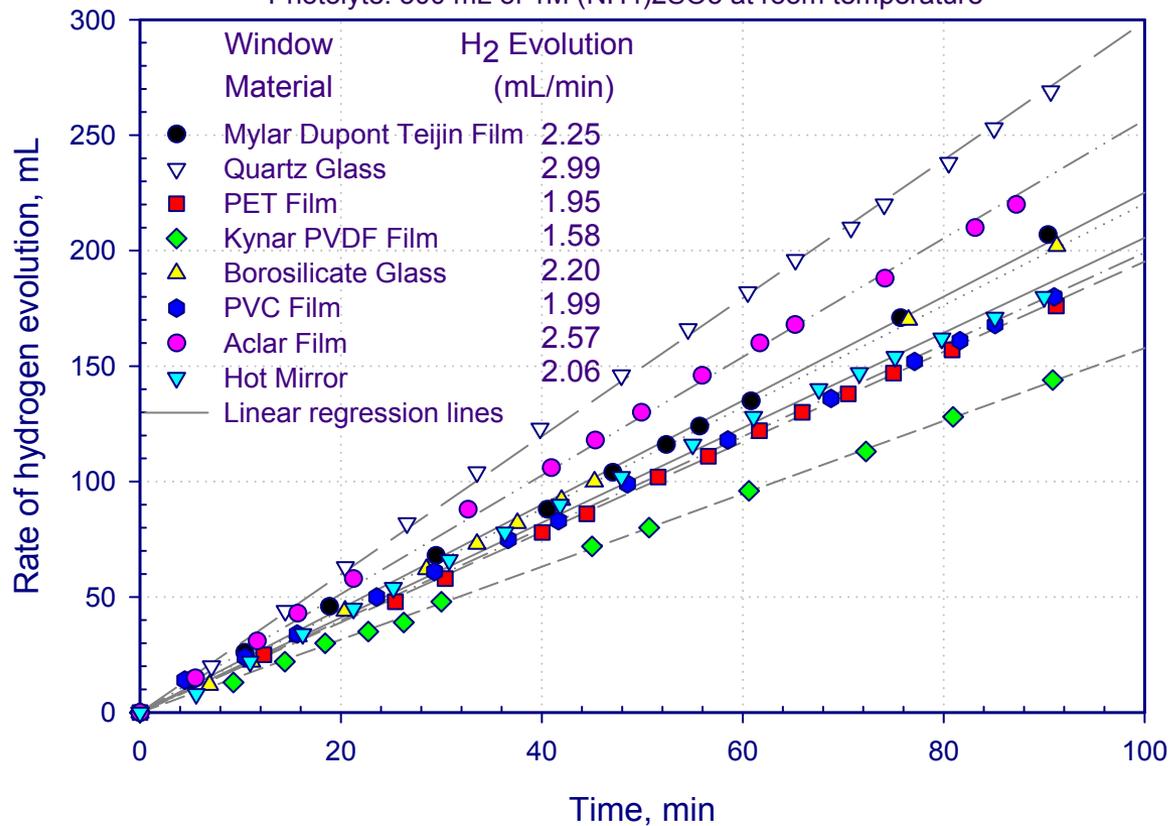
# Effect of Photocatalyst Doping



Photocatalyst: 0.5wt% NM on CdS; Photolyte: 1M  $(\text{NH}_4)_2\text{SO}_3$

# Effect of Photoreactor Window Material

Photocatalyst: 0.5 wt% NM (70%-Pt, 20%-Pd, 10%-Ru) doped CdS  
 CdS loading: 0.50 g  
 Photolyte: 300 mL of 1M (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> at room temperature



# Electro-oxidation of Ammonium Sulfite - Summary

| Cathode  | Cell Voltage (V)      |                            |                        |
|--|-----------------------|----------------------------|------------------------|
|  | 10 mA/cm <sup>2</sup> | 40 mA/cm <sup>2</sup>      | 100 mA/cm <sup>2</sup> |
| ELAT GDE   | 1.14                  | 1.40                       | 1.71                   |
| Ni mesh  | 1.50                  | 1.68                       | 2.29                   |
| Pt/Nb mesh   |                       | 1.95 @ 20°C<br>1.62 @ 60°C | 1.95 @ 60°C            |
| MEA, N112 (30 mg Pt/cm <sup>2</sup> )                | 1.01                  | 1.41 @ 20°C<br>1.21 @ 60°C | 1.50 @ 60°C            |
| MEA, N111 ( $\approx$ 2 $\mu$ g Pt/cm <sup>2</sup> ) |                       |                            | 1.40 @ 80°C            |

- Hydrogen produced quantitatively
- Very low Pt loading achieved
- Over-potential on anode side still very high
- Anode potential pH sensitive

# Mechanisms of ZnO/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> Decomposition

**Step 1 (T ~400-500°C):**



**Step 2 (T < ~900°C):**



**Step 3 (T > ~900°C):**



# Materials Challenges

- **Reduction or elimination of noble metal catalysts to reduce cost**
  - Reduce Pt by exchanging with less expensive NM (*e.g.*, Pd, Ru)
  - Non-NM dopants (*e.g.*, Cr, etc.)
- **Low-cost heliostat development**

# Challenges Facing Photocatalytic-SA Cycle Development

- **Noble metal loading**

- Photocatalyst is a bandgap semiconductor (CdS)
- Pt is 70% by wt. of NM loading and accounts for close to 60% of the total cost of chemicals & reagents utilized in the cycle

- **Potential solutions**

- Reduce Pt loading by mixing with co-catalysts (Ru, Rh) to optimize catalyst activity
- Exchange Pt for non-NM catalyst that is more cost-effective

# Other SA Cycle Issues Needing Refinement

- **Thermolytic reactors**

- **Low-temperature reactor (~500°C)**

- Ammonium sulfate reaction with ZnO to produce  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  &  $\text{ZnSO}_4$

- Mixing & reaction of solids with evolution of gases

- **High-temperature reactor (~900°C)**

- Decomposition of  $\text{ZnSO}_4$  to  $\text{ZnO}$ ,  $\text{SO}_2$  &  $\text{O}_2$

- Evolution of gases from solid reactant

# Potential Solutions/Approaches (1)

- **Low-temperature reactor design**
  - Conceptual designs include an unfired-boiler type reactor, with heat transfer oil flowing through pipes to heat the reactor
  - Some storage of hot oil would be possible for balancing reactors
  - Allows for easier sealing; no solar window needed
  - Receiver similar to LUZ – steel tubes with evacuated glass covers
  - Heliostats focused on receiver

# Potential Solutions/Approaches (2)

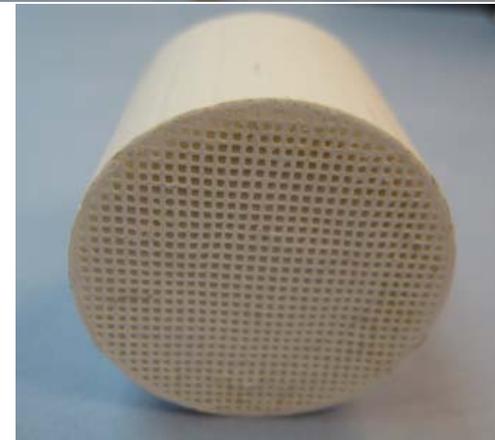
- **High-temperature reactor design**
  - Direct insolation with window to maximize receiver efficiency
  - Secondary reflector to reduce aperture
  - Heat recuperation between low- and high-temp reactors

# Potential Solutions/Approaches (3)

- **High-temperature reactor design**

- **Conceptual designs**

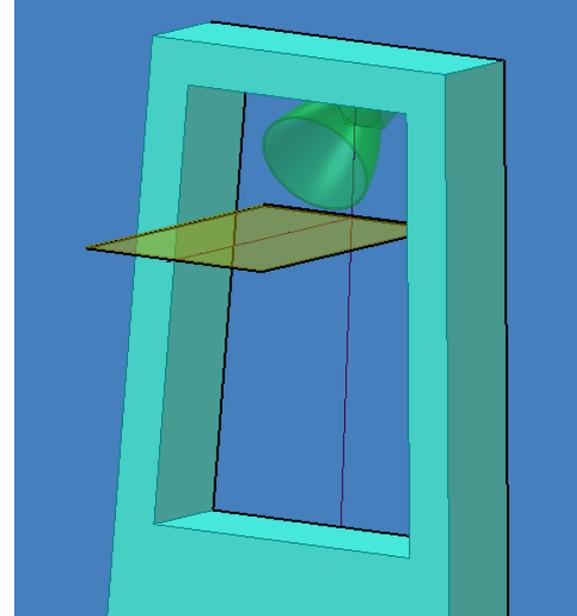
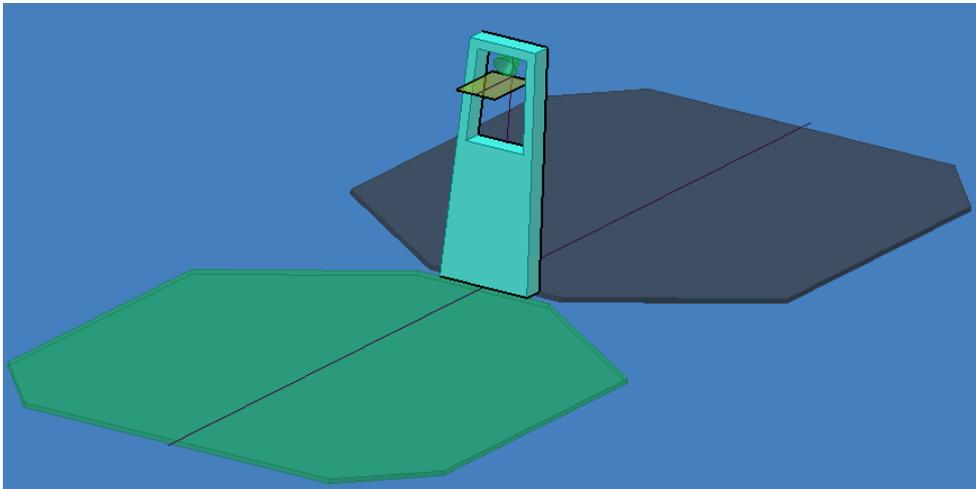
- Modified “bucket lift” with ceramic buckets & chain drive
- Rotating kiln with bulk solids heating
- Fluidized bed reactor using steam & ZnO-coated on alundum catalyst support supplied by Saint-Gobain NorPro (4-6 mm spheres)
- Spouted bed design (IMCC-US AEC)



# Solar Interface Options (1)

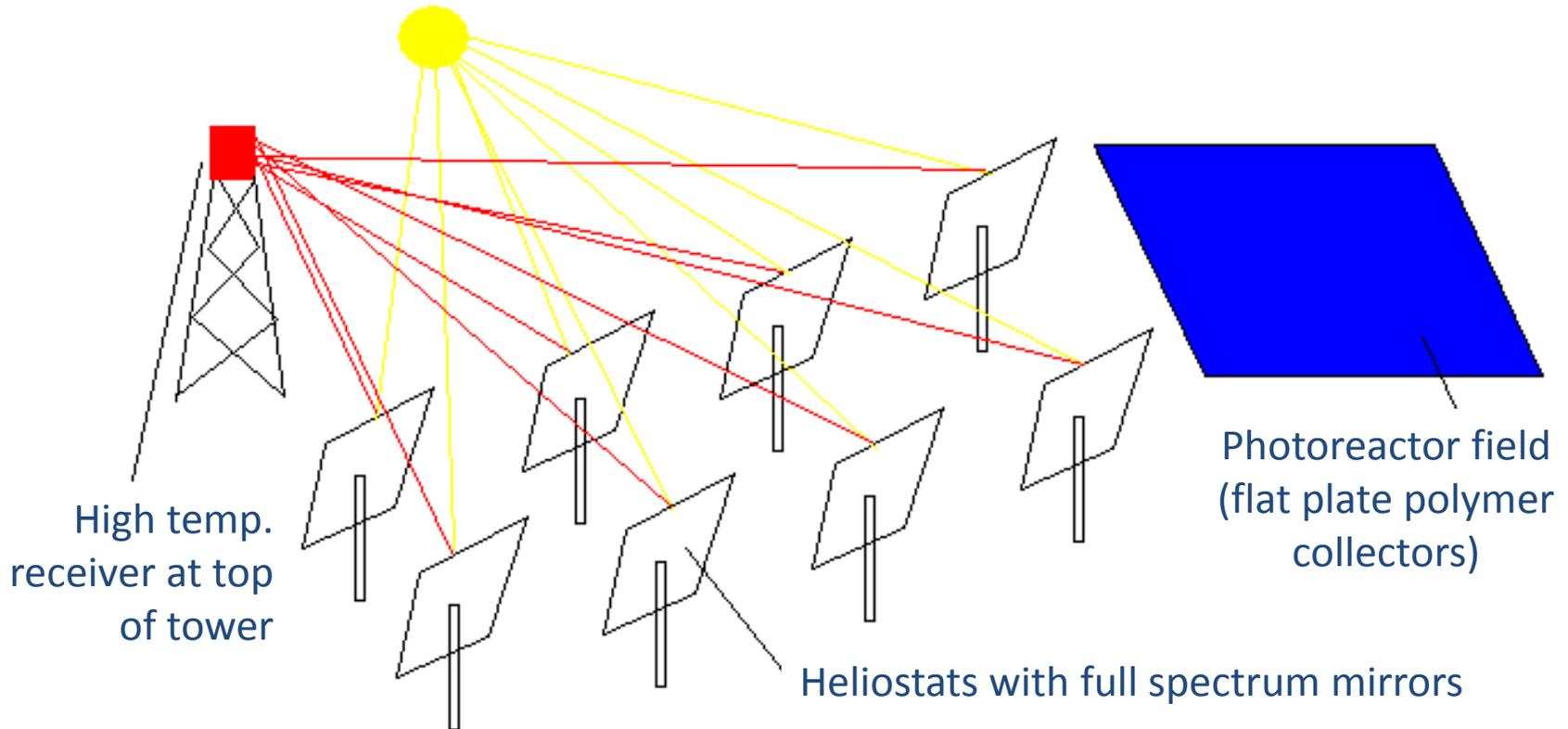
- **Cold Mirror Concept**

- North-field heliostats with full-spectrum reflectors
- Cold mirror near focus to redirect photonic flux down to two-sun photoreactor field South of tower



# Solar Interface Options (2)

- Separate thermal receiver & photoreactor fields – *i.e.* dual field (DF)



# Solar Interface Challenges (1)

- **Beam Splitting (BS) Options**
  - Hot mirrors require large areas of mirror and liquid/gas distribution/collection system over entire heliostat field → costly
  - Cold mirror near receiver can be 500X smaller and can reflect to two-sun photoreactor field to South, increasing solar efficiency and decreasing photoreactor size
  - Separate one-sun photoreactor field and thermal field uses ~30% fewer heliostats but wastes some sunlight (low efficiency)

# Solar Interface Challenges (2)

- **Solar Efficiency**

- Beam splitter gives higher overall solar efficiency, but requires ~30% larger heliostat field due to absorption losses and removal of UV/VIS energy from beam to thermal reactors
- Separate photoreactor field minimizes heliostat field size and simplifies systems but requires a large photoreactor field that “throws away” all but UV/VIS energy falling on it
- Heliostat field cost is the driving factor, favoring separate receivers for photocatalytic approach

# Solar Interface Challenges (3)

- **Photoreactor Design**
  - Low-cost “air mattress” design using PVDF (Kynar®) film for top surface
    - PVDF material has excellent UV transmittance in thin sheets
    - PVDF is tough and long-lived in outdoor exposure
    - PVDF is used extensively for outdoor exposure and for protection from UV damage (building facades, street coatings, etc.)

# Solar Interface Challenges (4)

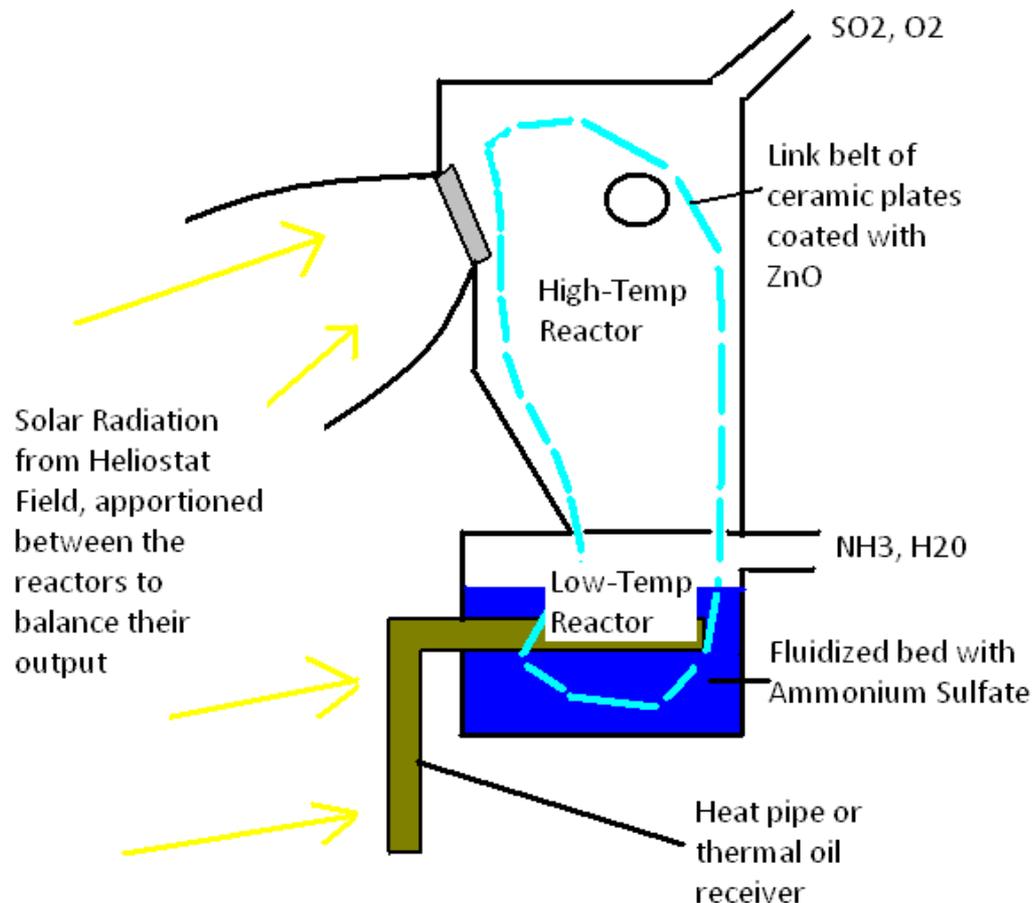
- **Process control of the thermal reactors is common to both the photocatalytic & electrolytic approaches**
  - **Reactors have different characteristics:**
    - Low-temp reactor operates at 500°C;  $\text{NH}_3$  can be reacted immediately to eliminate storage
    - High-temperature reactor operating temperature  $\sim 900^\circ\text{C}$ ;  $\text{SO}_2$  production must be balanced with  $\text{NH}_3$  from low-temperature reactor
  - **Storage as liquids is convenient & allows daylight-only operation of high-temperature reactors**
    - Avoids high-temperature storage
    - Direct absorption solar receivers are more efficient than storage/heat exchange

# Solar Interface Challenges (5)

- **Process control approach**
  - High-temperature receiver paces operation
  - Intermediate temperature thermal storage and movement of heliostats between high- and low-temp receivers to achieve balance in outputs
    - Store 500°C heat in early AM and late PM when high-temp reactor cannot operate
    - Proportion heliostats and use storage during day to match outputs of reactors

# Solar Interface Challenges (6)

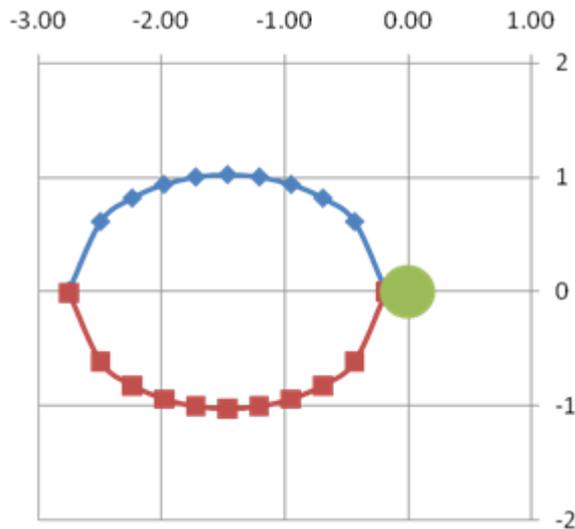
## • Example Reactor Configuration (Linkbelt)



- Low thermal inertia
- Output balanced by moving heliostat aim points
- Minimal ZnO inventory
- Heat recuperation between reactors
- Simple control by belt speed, heliostat illumination

# Heliostat Configuration

Photocatalytic system with cold mirror would use North-field heliostat configuration



Heliostat effectiveness including cosine, attenuation, and shading from tower

View area on ground from receiver CPC with 40 deg outlook angle and 30 deg acceptance half-angle (dimensions in tower heights)

