2005 DOE-NE Nuclear Hydrogen Initiative

Hybrid Sulfur Thermochemical Process Development

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Project PDP45

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Overview

Timeline

- Start Date: June, 2004
- End Date: September, 2005
- 75% Complete
- Follow-on to complete integrated lab demo to be funded for 10/05 – 9/08

Barriers

- Electrolyzer performance and cost
- High temperature materials
- Lower nuclear H_2 cost than solar TC goal of $3/gge at plant gate in 2015
- Proof-of-concept to meet MW-scale pilot plant decision by end of FY08

Budget

- Total funding (to date) - $480 K
- FY04 Funding - $180 K
- FY05 Funding - $300 K
- FY06 thru FY08 - TBD

Collaborators

- Univ. of So. Carolina - Electrolyzer
- Westinghouse Electric - consultation
- Proton Energy Systems – PEM Elec.
- Sandia National Lab and INL – H_2SO_4 loop development & catalysts

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Objectives

- To assist DOE-NE in selecting the preferred Thermochemical Cycle for integration with an advanced nuclear reactor
  - Develop a conceptual design for the Hybrid Sulfur thermochemical hydrogen production system, including preliminary flowsheet analysis, estimated system performance, and projected hydrogen production costs
  - Identify key technical issues and concerns, and prepare a development plan for a fully-integrated laboratory demonstration of the HyS Cycle
  - Perform proof-of-principle demonstration testing of an SO_2 anode-depolarized electrolyzer using a single-cell PEM-type water electrolyzer under near-ambient conditions

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Technical Approach

- **Create a high-efficiency process design for the Hybrid Sulfur thermochemical water-splitting cycle**
  - Update and improve original Westinghouse flowsheets
  - Use AspenPlus software to calculate mass and energy balances and to optimize system performance and H_2 cost
- **Develop and test a high-performance PEM-based electrolyzer using SO_2 anode depolarization**
  - Leverage PEM fuel cell and electrolyzer advancements to develop a low-cost H_2O/SO_2 electrolyzer achieving cell voltages of <0.6 volts per cell
  - Perform small-scale proof-of-concept testing beginning with a modified PEM water electrolyzer
  - Characterize performance, materials integrity, sulfur crossover, and effects of operating conditions (temperature, pressure, acid concentration)

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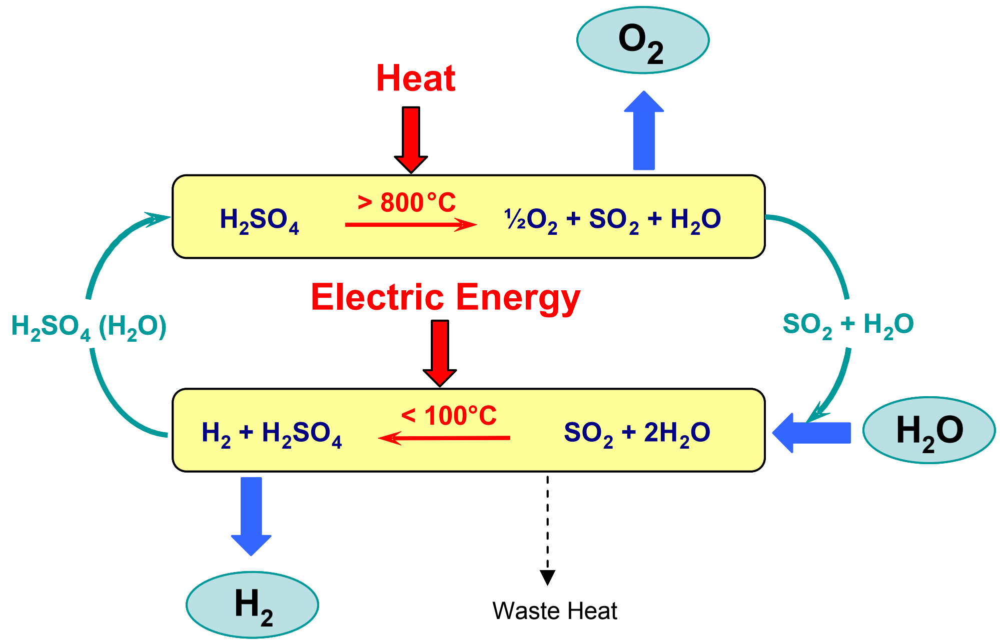
Accomplishments

- Conceptual Design Report Completed (4/1/05)
  - Improved system design with higher process efficiency of >50% (HHV)
  - SO_2-depolarized electrolyzer analysis performed; MEA/PEM concept selected; detailed development plan prepared
  - Key technical issues identified and approaches developed
  - Three patent disclosures prepared
- Ambient Pressure Electrolyzer Testing
  - Test plan prepared and issued
  - Test facility design completed; construction in progress
  - PEM-based SO_2-depolarized electrolyzer procured
- Electrolyzer Development and Integrated Testing
  - Integrated lab-scale test plan and conceptual design completed
  - High Pressure (20 bar) electrolyzer design scheduled for fourth quarter

Hybrid Sulfur Cycle

Inputs:
- Water
- Heat
- Electricity



Outputs:
- Hydrogen
- Oxygen
- Waste Heat

- Originally developed by Westinghouse Electric in 1973-1983
- Two-step hybrid thermochemical cycle; only S-O-H chemistry
- SO_2 anode-depolarization reduces reversible cell voltage to 0.17 VDC per cell (more than 85% less than pure water electrolysis). Practical voltages are 0.45 to 0.60 VDC per cell.

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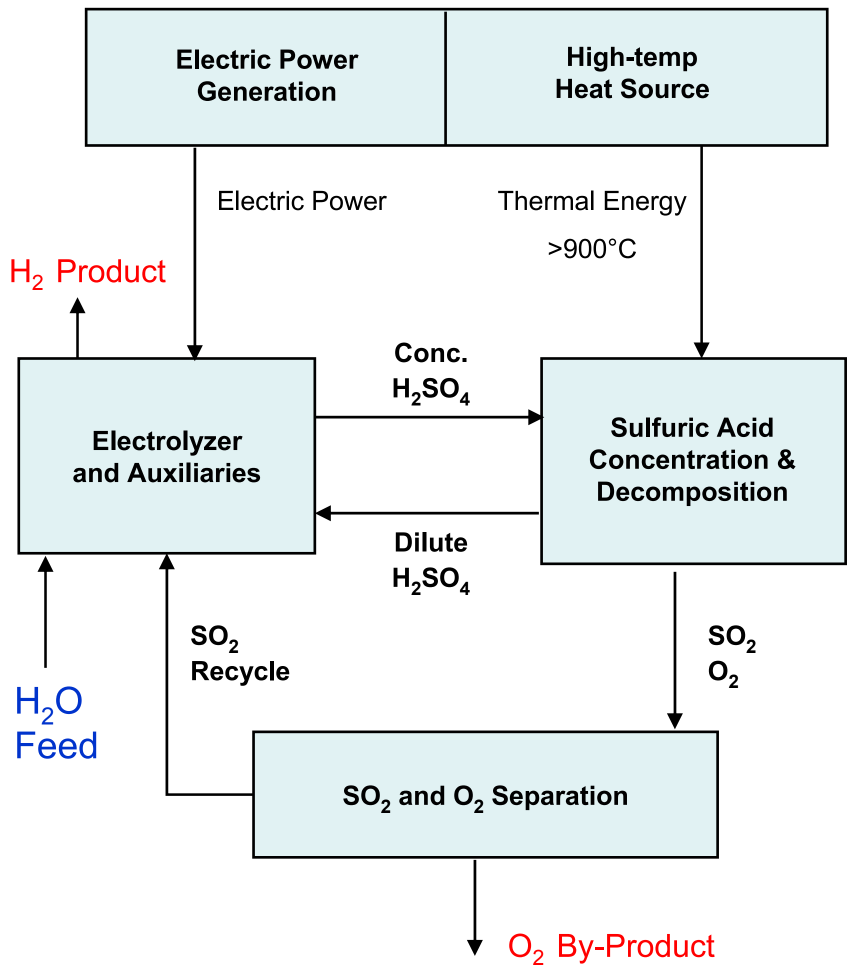
Processing Steps and Functions Defined

- High temperature (>900°C) heat source could be nuclear reactor or solar thermal
- Thermochemical system has three main processing units
  - SO_2-depolarized electrolyzers
  - Sulfuric Acid concentration and decomposition
  - SO_2/O_2 separation
- High Thermal Efficiency >50% (HHV basis) based on rigorous flowsheet modeling



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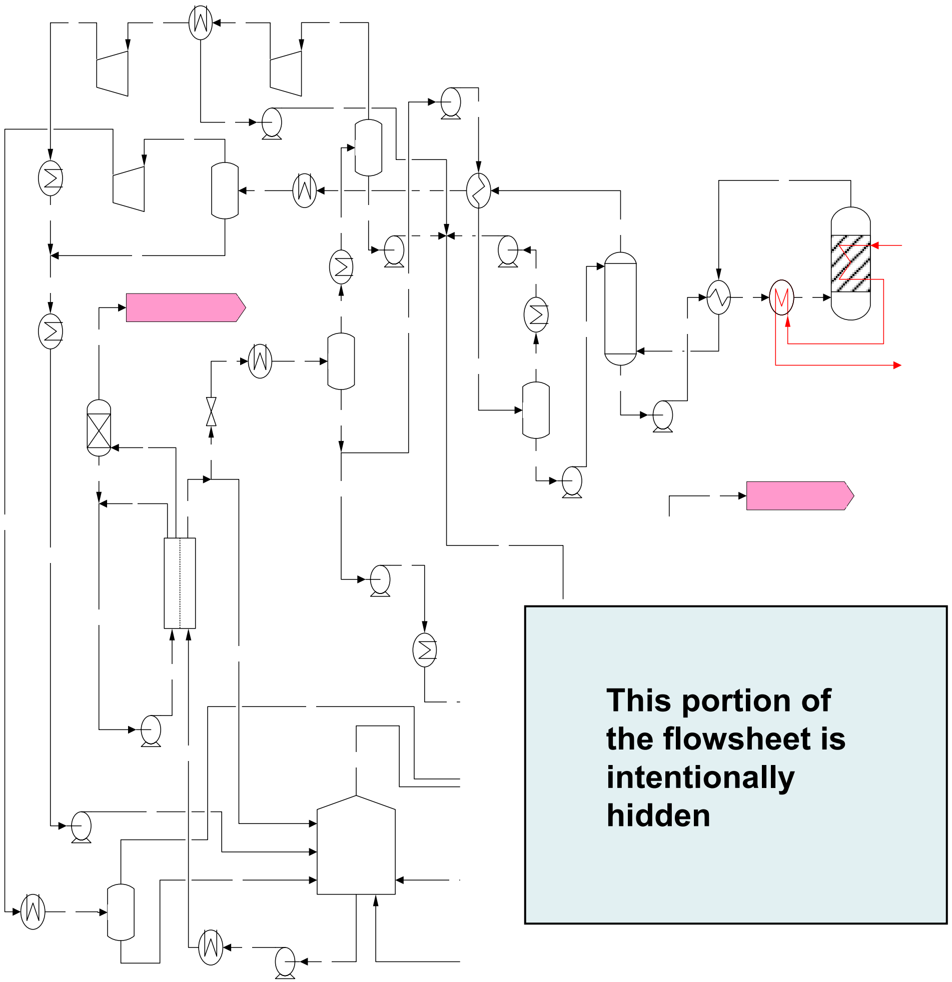
Process Design Optimized

- AspenPlus flowsheet, material and energy balances, performance, heat source integration, capital and production costs
- Performance goals set for electrolyzer; test data is needed for further design optimization
- Improved acid processing scheme developed (89% Section B thermal efficiency vs. previous 75%)
- High-efficiency SO_2/O_2 separation system developed (patent pending)
- Tradeoff studies in process for electrolyzer acid feed concentration, cell temperature and pressure, and acid decomposition temperature



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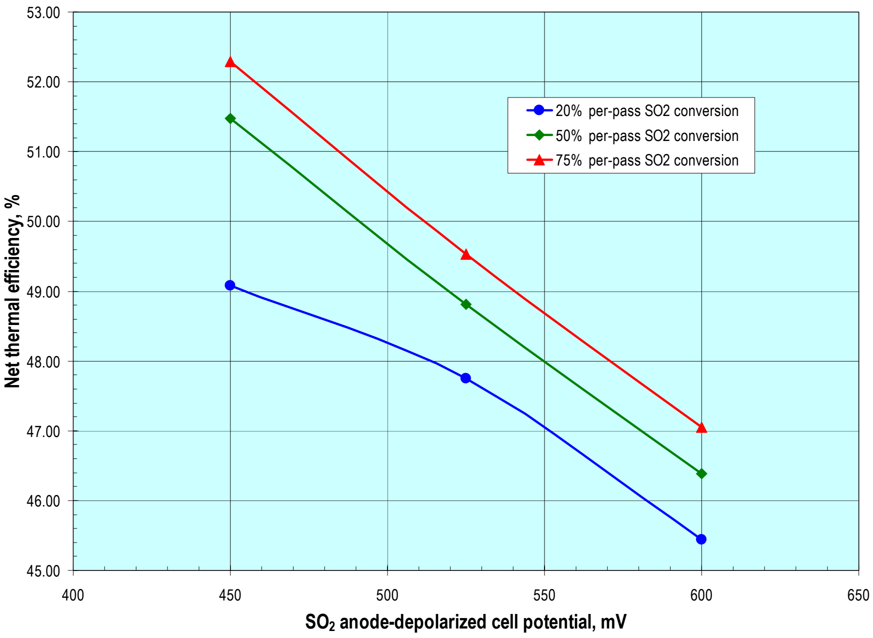
Tradeoff Studies

- Greatest performance uncertainty is with regard to electrolyzer efficiency
- High acid concentrations increase voltage (lower cell efficiency) but lower Section B thermal requirements
- Lower current densities reduce cell voltage but require bigger cells
- Other variables include T and P and SO_2 conversion per pass
- More experimental data is needed
- Sensitivity analysis shows overall plant thermal efficiency varies from 45.4% (20% conversion, 600 mV) to 52.3% (75% conversion, 450 mV)
- Higher temperature thermal input to Section B (>900°C) may permit greater total plant thermal efficiency

Overall HyS Plant thermal efficiency (HHV basis) vs. Cell Voltage for 900°C heat input



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Baseline HyS hydrogen production costs exceed goals and are less than SI Process

		SI*	HyS
Plant Rating	MW_{th}	2400	2400
Plant Efficiency	% (HHV basis)	52-42	48.8**
Hydrogen Output	Tonnes/Day	760-614	580
Electric Output	MWe	0	216
Reactor System Cost	$M	1,150	1,198
Electrolyzer Cost	$ per m^2	N/A	2000
Hydrogen Plant Cost	$M	819	516
Electricity @ 3¢/kWh	$M/yr	N/A	(51)
Total Annual Cost	$M/yr	413-399	306
Net Hydrogen Cost	$ per kg	1.65-1.98	1.60
- with O2 credit		1.36-1.69	1.31
DOE Solar Goal (2015)	$ per kg	3.00	3.00

*W.A. Summers et al., "Centralized Hydrogen Production from Nuclear Power: Infrastructure Analysis and Test-Case Design Study, Interim Project Report, Phase A Infrastructure Analysis", US DOE NERI Topical Report, Project No. 02-160, 07/31/2004

**Current flowsheet; >50% expected.

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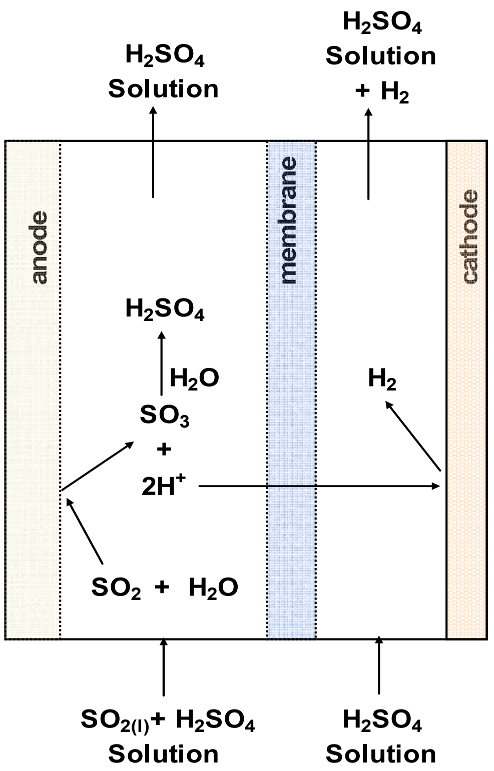
Electrolyzer Approach

- Anode feed consists of SO_2 dissolved in sulfuric acid
- Gaseous H_2 evolves on cathode
- Cathode can be dry or contain recirculating sulfuric acid
- Original Westinghouse cells used microporous rubber membranes
- Current concept will employ Nafion membrane in MEA/PEM arrangement
- Initial testing on water only showed current densities up to 1900 mA/cm^2



SO_2 anode-depolarized electrolysis

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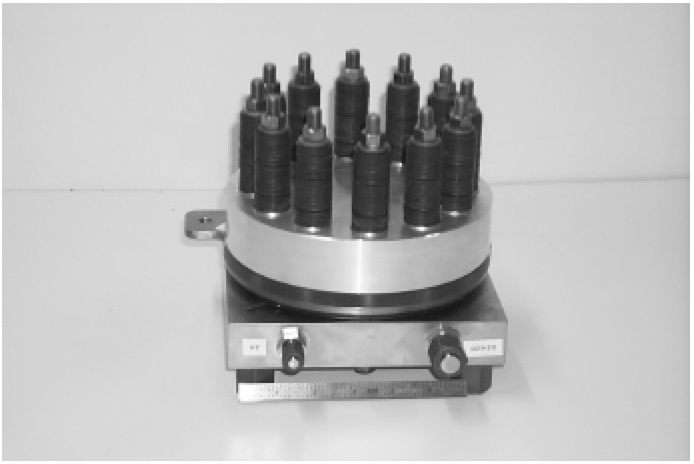
Ambient Pressure Testing of Electrolyzer

- Test Purposes
  - Verify reduced cell voltages based on SO_2-depolarization
  - Verify applicability of MEA and PEM concepts
  - Examine issues of SO_2 crossover and cell degradation with time
  - Acquire data for modeling and system scale-up
- Experimental Status
  - Test plan prepared
  - Awaiting completion of test facility



Modified PEM Water Electrolyzer
($84\ cm^2$ active cell area)

(Manufactured by Proton Energy Systems, Inc. with SRNL specified materials and changes)

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Test Facility in Progress

- Design complete and all equipment on hand
- Operating plan and safety analysis completed
- Final approvals in progress
- Shakedown testing planned for mid-May

Fume Hood for installation of SO_2 anode-depolarized electrolyzer tests

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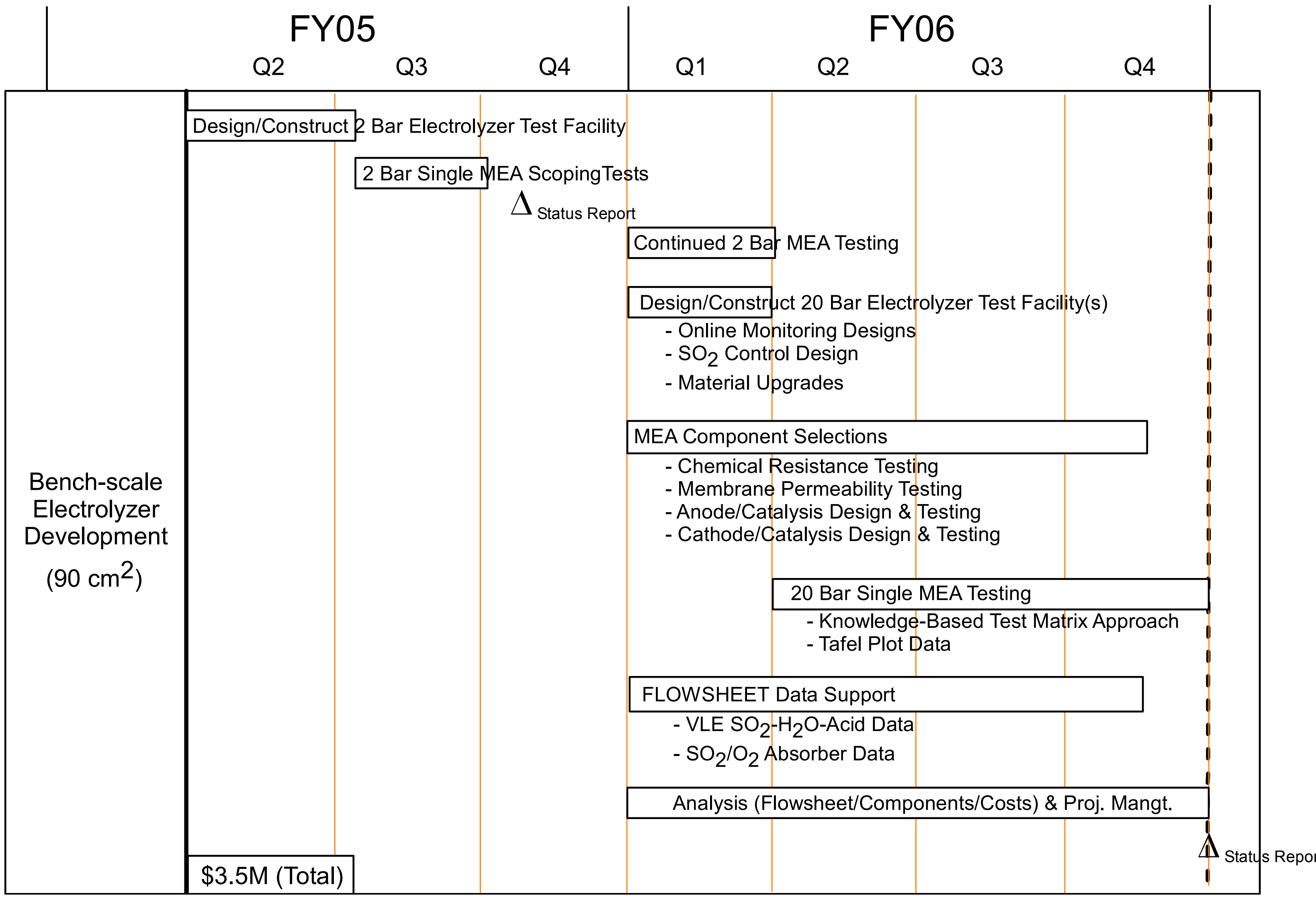
Bench-Scale Electrolyzer Development Schedule



Technical Issues and Concerns

- Compatibility of MEA/PEM design with operating conditions
- Prevention of SO_2 crossover to cathode (i.e. sulfur deposits)
- Need for better data on SO_2 solubility in sulfuric acid
- Material selections for MEA components
- Electrocatalyst type and loadings
- Effect of increased operating pressure on SO_2 solubility and electrolyzer performance
- Tradeoff study on operating pressure/temperature and sulfuric acid concentration; flowsheet optimization
- Verification of improved SO_2/O_2 separation design
- Integration with SI-developed acid decomposition system

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Response to Previous Year Reviewers' Comments

- Not Applicable
- This is the first year this project has been reviewed

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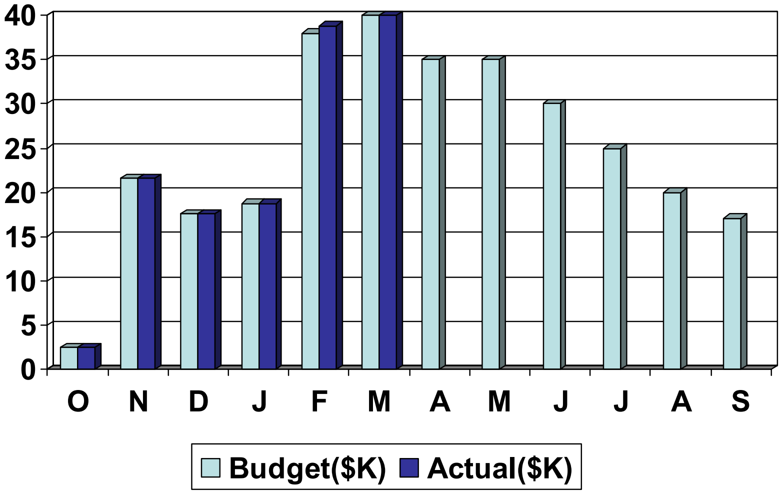
Milestone Status and Project Issues

Milestones

- Test Plan for Small Single Cell Electrolyzer(M3) – 3/1/05 (Completed)
- Conceptual design for HyS including efficiency estimate(M3) -4/1/05 (Completed)
- Characterization Testing of H20-SO2 Electrolyzer(M2) – 8/1/05 (On Schedule)
- Design Small Single Cell Pressurized Electrolyzer(M3) – 9/15/05 (start 6/1/05)

Issues

- FY06 funding needs to be substantially increased for this process to be ready for the pilot plant decision by end of FY08



Total FY05 Funding = $300 K

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Future Plans

- **FY05 Second Half**
  - Assemble test facility and initiate shakedown testing
  - Baseline testing with water followed by water/SO_2
  - Characterization testing with various sulfuric acid concentrations and operating temperatures
  - Duration testing up to 100 hours
  - Prepare pressurized electrolyzer design
- **FY06 Proposed**
  - Design and construct pressurized (20 bar) electrolyzer and test facility
  - Perform system analysis and flowsheet improvements

Publications and Presentations

1. W. A. Summers, "Hybrid Sulfur Thermochemical Process", DOE Office of Nuclear Energy, Science and Technology, Semi-annual Program Review, Washington, DC, September 21, 2004.
2. M. R. Buckner, "Hybrid Sulfur Thermochemical Process", DOE Office of Nuclear Energy, Science and Technology, Semi-annual Program Review, Washington, DC, March 10, 2005.
3. M. R. Buckner et al, "Conceptual Design for a Hybrid Sulfur Hydrogen Production Plant", prepared for DOE Office of Nuclear Energy, Science and Technology under appropriation AF38, Nuclear Hydrogen Initiative, Savannah River National Laboratory Report No. WSRC-TR-2004-00460, April 1, 2005.
4. M. B. Gorensek, W. A. Summers and Mr. R. Buckner, "Conceptual Design for a Hybrid Sulfur Thermochemical Hydrogen Process Plant", AIChE Spring 2005 National Meeting, Atlanta, GA, April 13, 2005

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Hydrogen Safety

- **The most significant hydrogen hazard associated with this project is:**

  The wide range of flammability limits for hydrogen in air, from 4% by volume to 74.5% by volume. Hydrogen leaks from a poorly designed experiment could cause an invisible flame, deflagration or even detonation, potentially resulting in personnel burns or equipment damage.

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Hydrogen Safety – Our approach to deal with this hazard is:

- SRNL requires that all laboratory work be reviewed using the copyrighted SRNL Conduct of R&D Manual. This process includes performing hazard assessments and mitigation analyses prior to the start of any laboratory work.
- Specific procedures for this project include:
  1. Operate in a well ventilated chemical hood that will maintain the hydrogen concentration well below the lower flammability limit, even with an equipment failure.
  2. Use components and piping rated for the pressure.
  3. Work with a hydrogen production rate of only two grams per hour.
  4. Operate using a detailed and peer reviewed Work Instruction.
  5. Always have at least two people present in the laboratory when work is being performed that has the potential to release hydrogen.
  6. Restrict access to the laboratory with a door lock and restrict access to the hood area with a railing.

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