Hybrid Sulfur Thermochemical Cycle

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2009 Annual Merit Review

Project PD_13_Summers

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Overview

Timeline

Start Date: June, 2004

End Date: Sept, 2009

80% Complete

Barriers

H. Electrolysis System Efficiency

U. High-temperature thermochemical technology

V. High-temperature robust materials

Budget

Total Project Funding

- DOE Share = $5.2 M
- Industry Cost Share = $140 K

FY08 Funding = $1052 K

FY09 Funding = $1325 K

Partners

Westinghouse Electric, PBMR, Shaw, Technology Insights

Giner Electrochemical (subcontract)

Univ. of South Carolina (U-NERI)

Sandia National Laboratory

DuPont, Vanderbilt, CWRU, Clemson

Project Objectives - Relevance

Goal: Develop Hybrid Sulfur thermochemical cycle as a viable option for large-scale hydrogen production using nuclear energy

Relevance:

- Permits large-scale centralized hydrogen production from water with no greenhouse gas or other harmful emissions
- Development of HyS Cycle can also be applied to hydrogen production from central solar receiver system
- Creates opportunity for transition by developing new non-fossil hydrogen option for large-scale industrial users

FY09 Objectives - Relevance

Overcoming Barriers:

- Key Step in HyS Cycle is electrochemical water-splitting based on use of an SO_2 depolarized electrolyzer (SDE)
- FY09 Objectives are focused on improving performance and operating lifetime of SDE using a PEM-type cell
- High temperature portions of HyS Cycle are common with Sulfur Iodine Cycle and are being developed in parallel with this project
- System design and economics have been performed in conjunction with industry to ensure relevance and to establish realistic performance and cost goals

Project Approach

- Select electrolyzer design approach meeting goals and performance targets (PEM-type cell selected)
- Conduct Component Development tasks to identify membrane, electrocatalysts and other key cell features, including materials and operating conditions. Verify in button-cell tests.
- Build and operate single cell test facilities at prototypical T&P
- Conduct proof-of-concept tests leading to lifetime tests on single cell electrolyzer of approximately 60-cm^2 active area
- Scale-up to multi-cell stacks and larger cell sizes
- Work with partners on alternative approaches

FY09 Research Plan - Approach

Component Development

- Establish key partnerships with PEM developers to leverage other work
- Use button-cell and specialized equipment to investigate improved membranes that reduce cell voltage and minimize sulfur crossover
- Continue investigation of electrocatalysts

Single Cell Testing

- Build and test alternative single cell electrolyzers (60-cm^2)
- Develop operating methods to prevent sulfur crossover
- Automate test facility and run long-term tests

Alternative Cell Approaches

- Work with industry and university partners on alternative cell design, including a Gap Cell and an anhydrous SO_2 cell

Approach - Milestones

FY08 – Third and Fourth Quarter

- Complete multi-cell stack testing (Level 1) (3/31/08)	**Complete**
- Complete mid-year evaluation for membranes and electrocatalysts (5/15/08)	**Complete**
- Issue final membrane characterization report (9/1/08)	**Complete**
- Complete Phase II single cell SDE testing and issue report (9/15/08)	**Complete**
- Issue Gap-cell report (9/15/08)	**Complete**

All FY08 Milestones were met on time or ahead of schedule

Approach - FY09 Milestones

FY09 Milestones

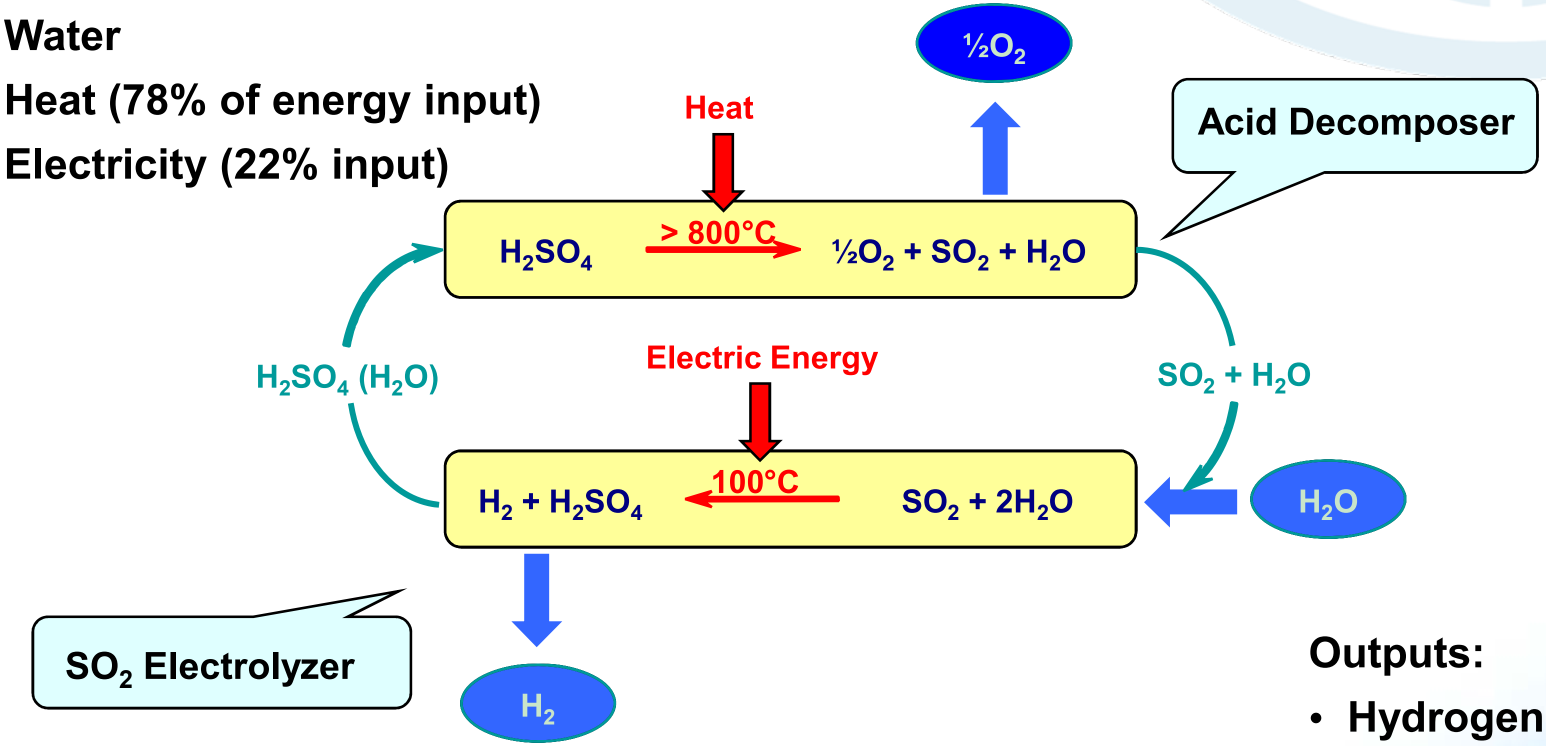
● Conduct SDE Technical Workshop (5/15/09)	**On Schedule**
● Level 1: Demonstrate SDE operation without sulfur buildup limitations (6/30/09)	**On Schedule**
● Complete Gap Cell Assessment (8/30/09)	**On Schedule**
● Complete 200 hour Single Cell test (9/15/09)	**On Schedule**
● Complete Button-cell Testing and Issue Component Development Report (9/15/09)	**On Schedule**

Hybrid Sulfur Process

The only 2-step, all-fluids thermochemical cycle – based on sulfur oxidation and reduction; only S-H-O compounds

Inputs:

- **Water**
- **Heat (78% of energy input)**
- **Electricity (22% input)**

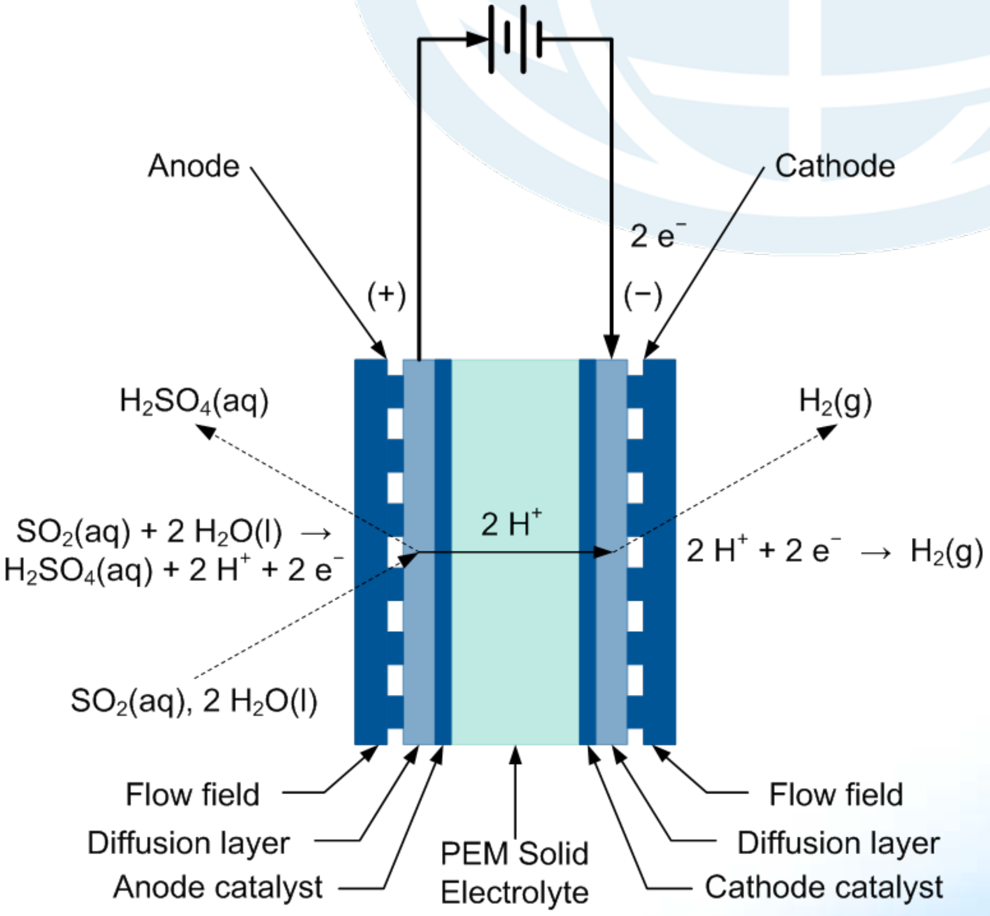


Outputs:

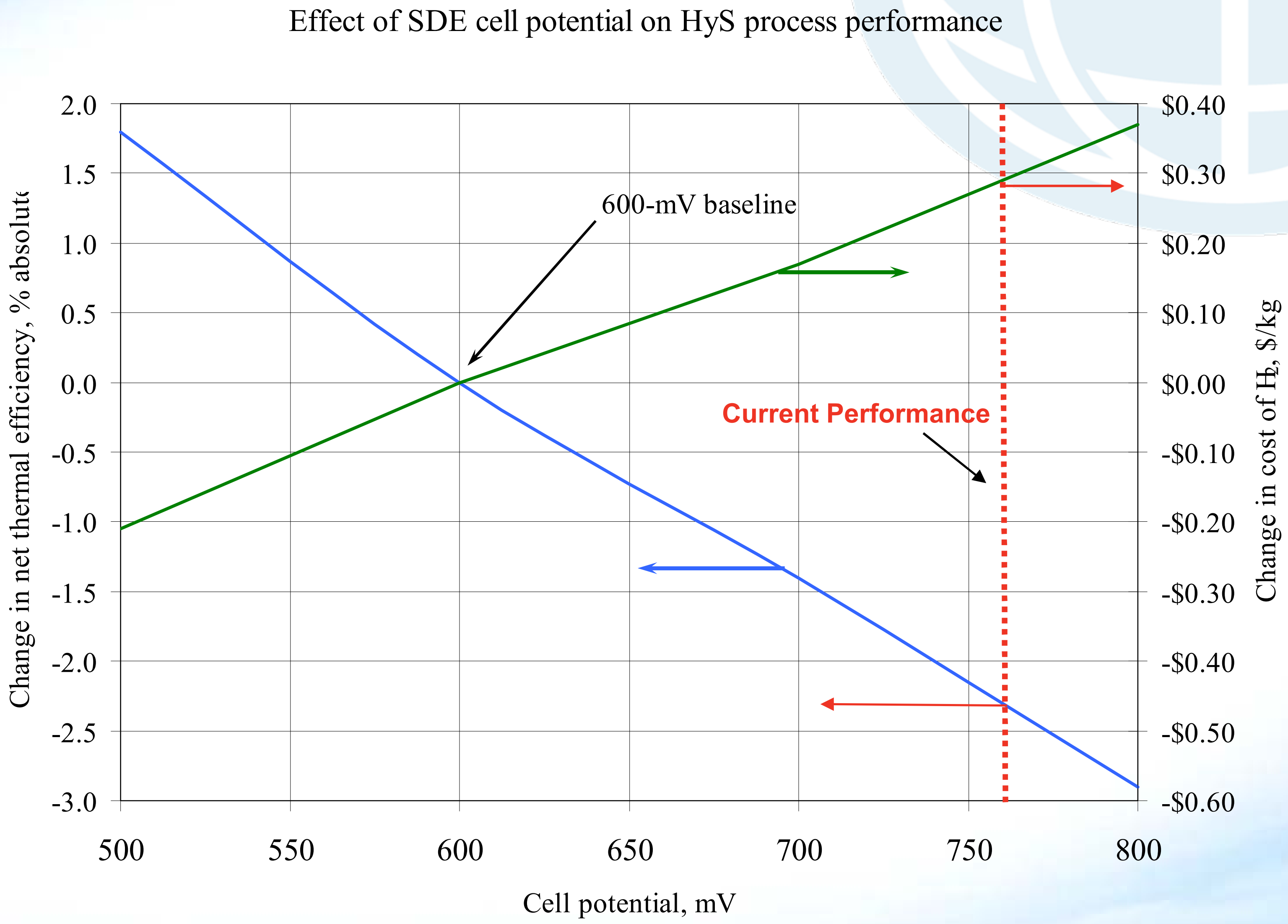
- **Hydrogen**
- **Oxygen**
- **Waste heat**

SRNL PEM Electrolyzer Concept

- SO_2 oxidized at anode to form H_2SO_4 and hydrogen ions
- Reversible cell potential reduced by 87% compared to water electrolysis (0.158V vs. 1.229V)
- PEM cell permits compact design, reduced footprint, and lower cost
- Target cell potentials of 600 mV @ 500 mA/cm² established
- Current HyS flowsheet based on operation at 100-120°C and 20-25 bar with 50 wt% H_2SO_4



Improved cell voltage reduces plant efficiency and hydrogen costs, but it is not the major driver



Reduction of Sulfur Deposition is a Key Technical Objective

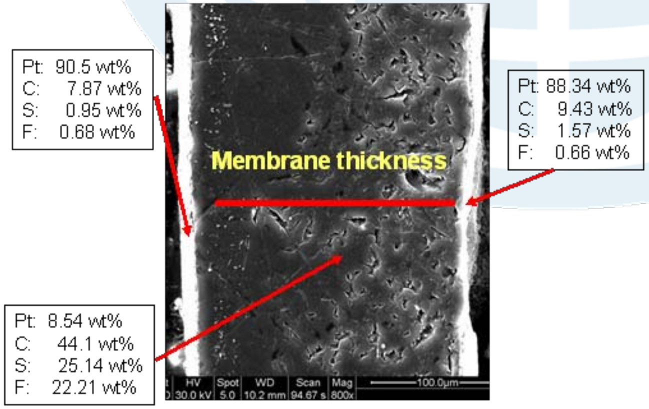
SO_2 can diffuse thru PEM from anode to cathode

Reduction at cathode can result in S deposits and physical damage to cell

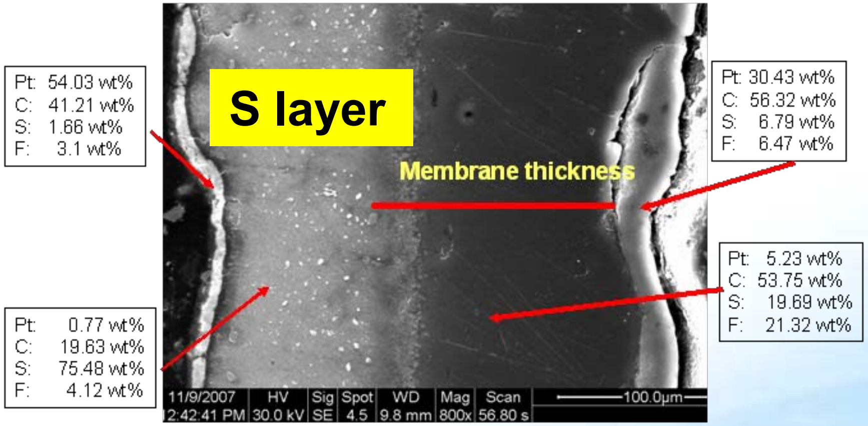
Certain designs and operating conditions avoid deposits

Multiple approaches

- Modify membrane
- Modify operating conditions
- Alternative cell designs



MEA 9, N117 with Pt black catalyst



MEA 20, N115 with Pt/C catalyst

Technical Accomplishments - Summary

- Completed major design study with industry
- Completed multi-cell stack test (Level 1 milestone)
- Tested ionic conductivity, SO_2 diffusion and chemical stability of over 15 membrane candidates
- Completed testing of six additional (32 total) single cell electrolyzers: <u>Developed new operating method to prevent sulfur crossover in cell</u>
- Upgraded test facility for unattended operation
- Developed gap cell with testing in progress

Nuclear hydrogen plant design, detailed HyS flowsheet and cost estimate completed with industry partners (Westinghouse, PBMR, Shaw)

Key design improvements:

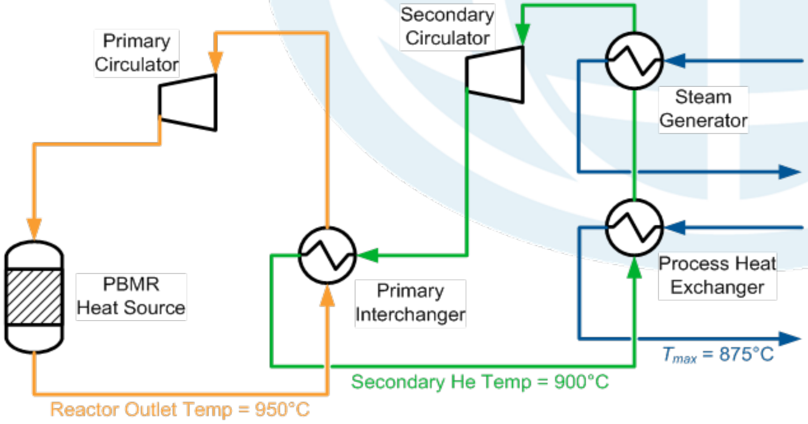
Optimized heat integration between reactor, hydrogen plant and bottoming cycle

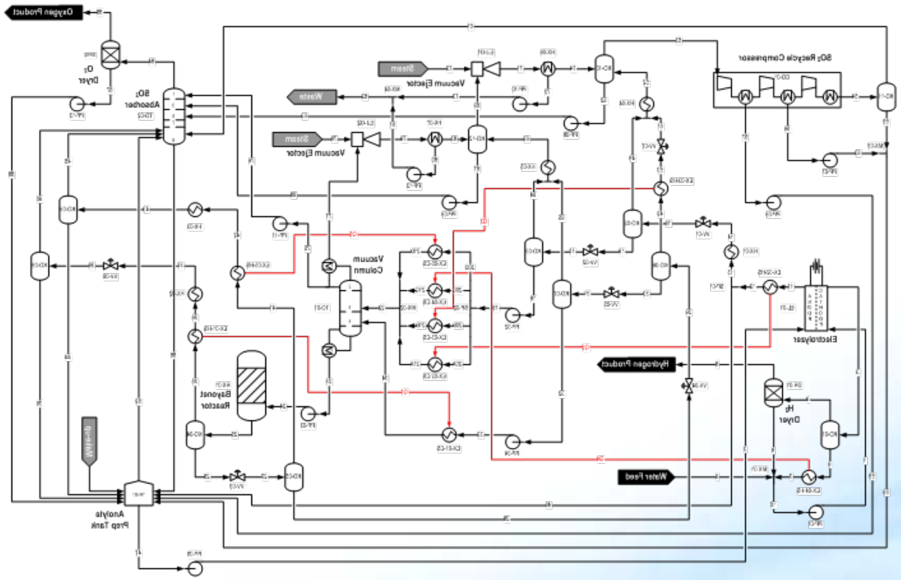
Improved thermal efficiency for HyS thru pinch analysis

Increased hydrogen production per PBMR by over 150%

Overall process efficiency = 37% (over 40% more H2 than conventional reactor+elect.)

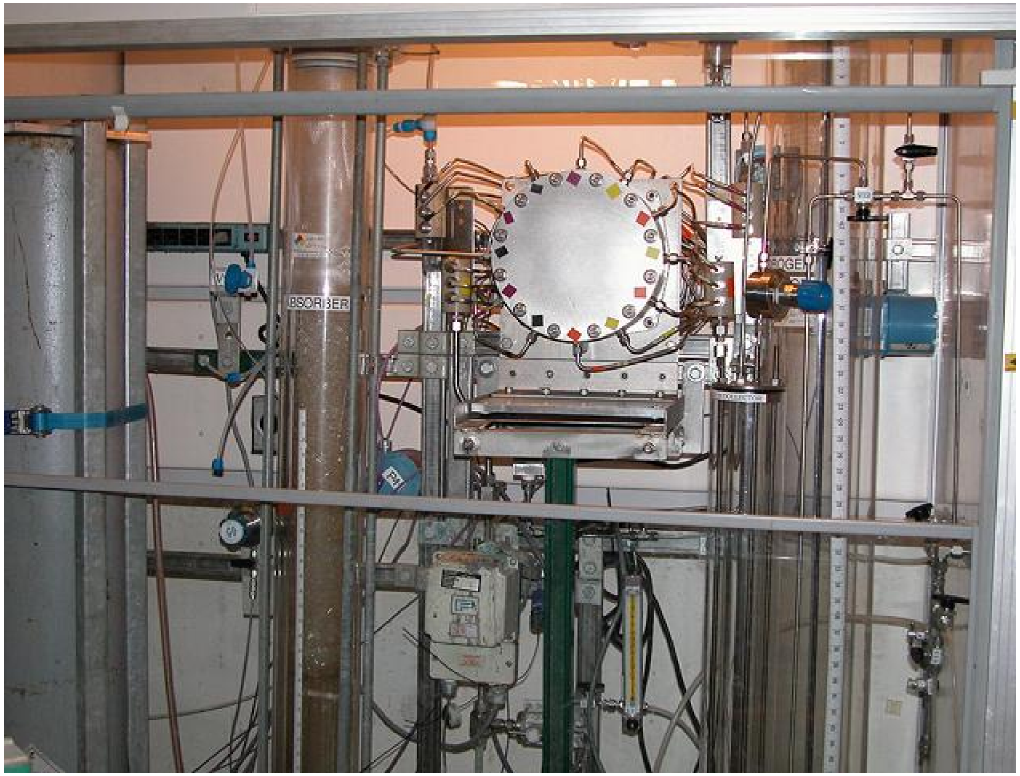
Capital costs and cost of hydrogen estimated w/H2A; Baseline = \$5.34/kg with range of \$4.15 - \$7.10/kg

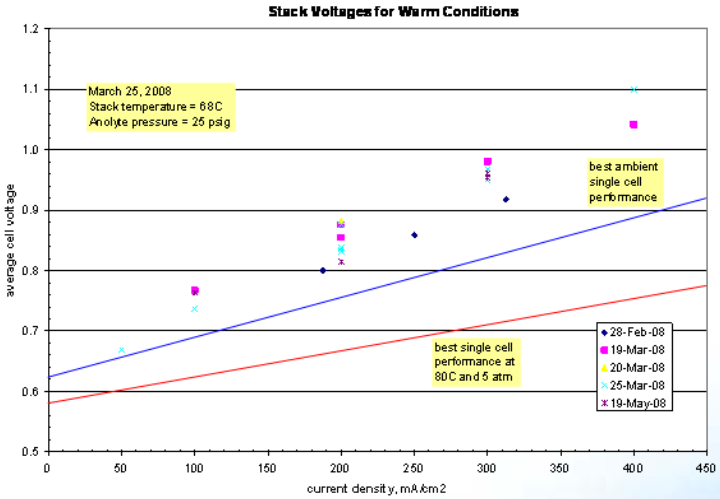




Multi-Cell Stack Testing Completed

- **Level 1 Milestone Completed on 3/26/08 (ahead of schedule)**
- **Demonstrated 86 lph H2 (8x scale-up) and multi-cell stack capability**
- **Key step leading to larger scale demonstration plant**





Electrolyzer Component Development Objectives

Proton Exchange Membrane

- Minimal SO_2 Transport
- Maximum ion conductivity

Anode

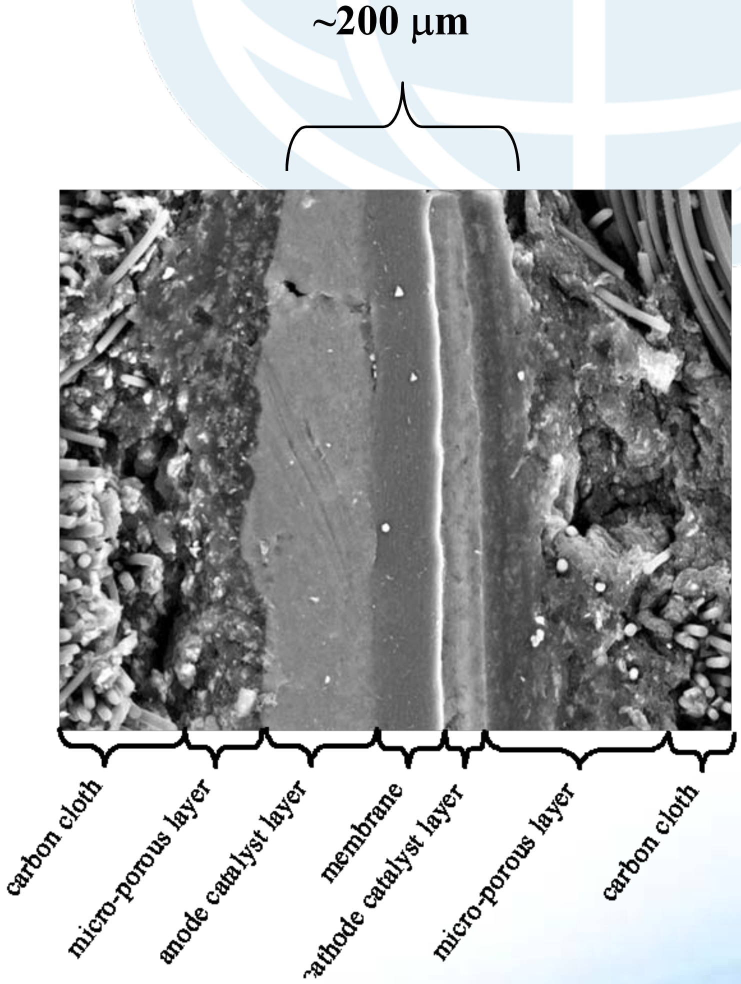
- Maximum SO_2 oxidation kinetics
- Minimal attack by SO_2/H_2SO_4

Cathode

- Maximum hydrogen formation kinetics
- Minimal reaction with SO_2

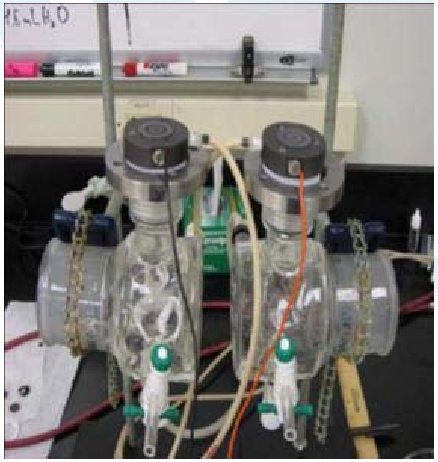
Flow Field/Diffusion Media

- Maximize SO_2 transport to anode
- Low pressure drop
- Chemically and mechanically stable

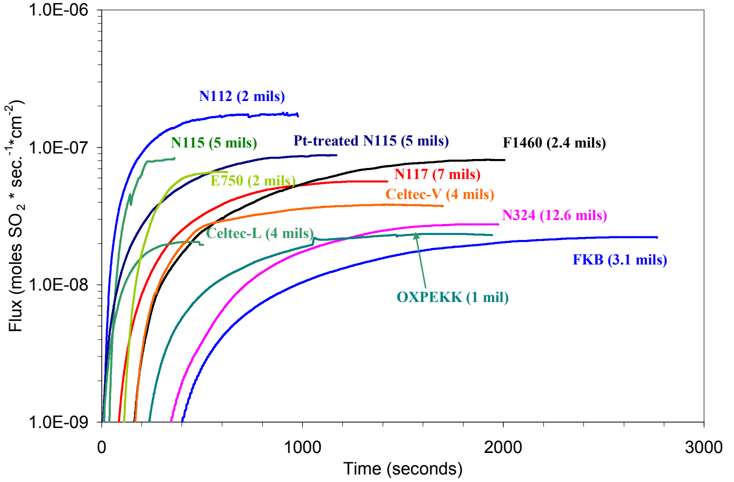


Improved performance obtained with new membranes

- Tested over 15 different PEMs
- All membranes exhibit reasonable ionic conductivities in 30 wt% H_2SO_4
- Established SO_2 mass transport for baseline PFSA membrane (Nafion®115)
- Pt-treated Nafion®, modified Nafion®, PBI, SDAPP, S-FPCB and PFSI membranes exhibit reduced SO_2 transport and good chemical stability in H_2SO_4
- PEEK and SPEEK membranes exhibit reduced SO_2 transport but poor chemical stability in H_2SO_4



Button-cell Electrolyzer

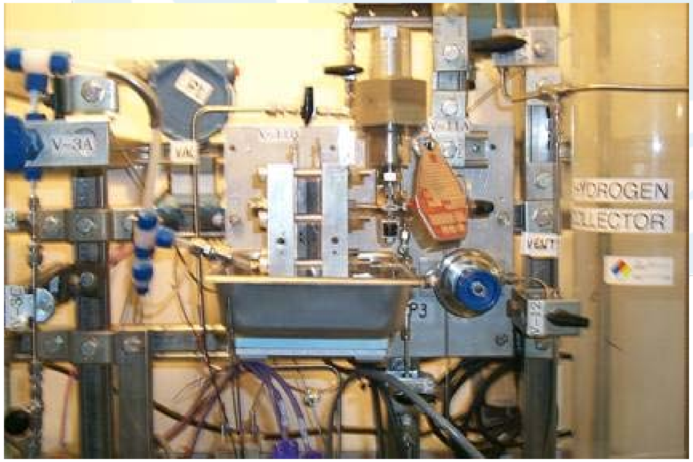


SO2 transport thru Experimental Membranes

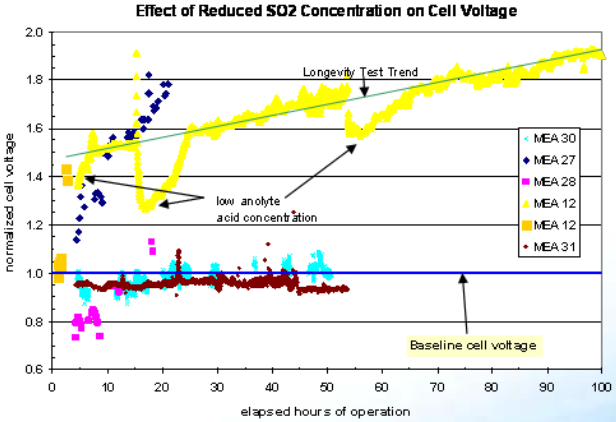
Key Findings: Advanced membranes can improve conductivity/SO_2 transport ratio by >8 times. Higher temperature operation (>100 C) can reduce cell voltage.

Single-cell Testing without Sulfur Build-up

- Developed new method of operating cell in SO_2-limited condition to prevent S crossover
- Completed 50 hour test run with no indication of sulfur
- Other qualitative measures also indicated reduced sulfur at cathode
- Test facility being modified for unattended operation to permit long-term testing
- Expect further improvements with advanced membranes and higher temperature operation
- Major step in development of SO_2-depolarized electrolyzer



Single Cell Electrolyzer (60 cm^2 active area)



SO_2-limited Cell Operation

Collaborations

- **Giner Electrochemical**
  - Industry subcontractor; multi-cell stack fabrication; gap cell development; button-cell test facility fabrication
- **Membrane developers**
  - Sandia National Lab, Clemson Univ., Vanderbilt, CWRU, Penn State, Univ. of So. Carolina, BASF, Giner, DuPont
- **Commercial nuclear plant developers**
  - Westinghouse Electric, Pebble Bed Modular Reactor (RSA), Shaw Stone and Webster. Earlier work: General Atomics, AREVA
- **Related work on solar-heated HyS Cycle**
  - Sandia National Laboratory, General Atomics

Future Work

FY09

- Perform extended operating tests (200-500 hours) on single cell electrolyzer to verify sulfur-free operation (Note: This is a DOE-NE Level 1 milestone)
- Continue membrane testing and select membranes for future testing in single cell electrolyzer
- Construct and operate a pressurized button-cell test facility permitting high temperature operation
- Continue work with industry, lab and university partners on membranes and alternative cell design approaches

FY10:

- Ongoing work will depend on DOE-NE down-select and the future of Nuclear Hydrogen Initiative program
- If funded, next key step is design and construction of an Integrated Lab-Scale Experiment of HyS, including high temperature acid decomposition and SO_2/O_2 separation

Summary

Relevance **HyS combined with advanced nuclear reactors (or solar receivers) can be an important source of hydrogen for industry and the transportation sector**

Approach **Establish system goals with industry partners. Leverage ongoing PEM fuel cell work and collaborate with membrane developers. Maintain strong component development efforts while advancing testing of larger cells and stacks**

Technical Accomplishments **Multi-cell stack demonstrated; high efficiency HyS commercial flowsheet completed; new membranes identified; test facility modified for unattended operation; successful method developed for sulfur-free operation**

Collaborations **Active partnership with commercial nuclear team on plant design; partnership with Giner on electrolyzer manufacture; collaborations with industry and university partners on membranes**

Future Work **Verify sulfur-free operation with extended testing; demonstrate complete cycle in an integrated lab-scale experiment**