Hybrid Sulfur Thermochemical Process Development

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DOE Hydrogen Program
2008 Annual Merit Review
Project PD26

This presentation does not contain any proprietary, confidential or otherwise restricted information

Overview

Timeline

- Start Date: June, 2004
- End Date: Sept, 2010
- 50% Complete

Budget

- Total Project Funding
  - DOE Share = $3.9 M (thru FY08)
  - Industry Cost Share = $140 K
- FY07 Funding = $1400 K
- FY08 Funding = $1000 K

Barriers

- U. High-temperature thermochemical technology
- V. High temperature robust materials
- NHI Objective – By 2019, operate a nuclear hydrogen production plant to demonstrate technical feasibility and cost competitiveness

Partners

- Westinghouse Electric
- Giner Electrochemical (subcontract)
- Univ. of South Carolina (U-NERI)
- Sandia National Laboratory (membrane & acid system develop.)

Objectives

- **The main focus of this project is to develop and demonstrate the Hybrid Sulfur thermochemical process as a viable option for large-scale hydrogen production using nuclear energy***
- **FY08:** Development and testing of an SO_2 depolarized electrolyzer (SDE) using PEM-type cell design
  - Optimize HyS process design, update flowsheet and perform cost analysis in conjunction with industry partner
  - Continue to identify and develop improved cell components to reduce sulfur crossover and increase cell efficiency
  - Conduct single cell SDE tests at elevated temperature and pressure
  - Install and test a multi-cell SDE with 100 lph hydrogen capacity

*Can also be driven by heat from central solar receiver system

Milestones

- **FY07**
  - Complete 100 hour single cell longevity test (5/15/07) — Complete
  - Complete construction of multi-cell stack (9/15/07) — Complete
- **FY08**
  - Complete HyS flowsheet and process design (3/15/08) — Complete
  - Complete multi-cell stack testing (3/31/08) — Complete
  - Complete mid-year evaluation for membranes and electrocatalysts (5/15/08) — Complete
  - Complete Phase II single cell SDE testing (9/15/08) — On Schedule
  - Complete component development and issue report (9/15/08) — On Schedule

FY08 Plan and Approach

Our approach is to analyze the overall Hybrid Sulfur process design and requirements and to perform development on the key new component, the SO_2-depolarzied electrolyzer. We try to maximize use of results and experience from programs on PEM fuel cells and PEM electrolyzers.

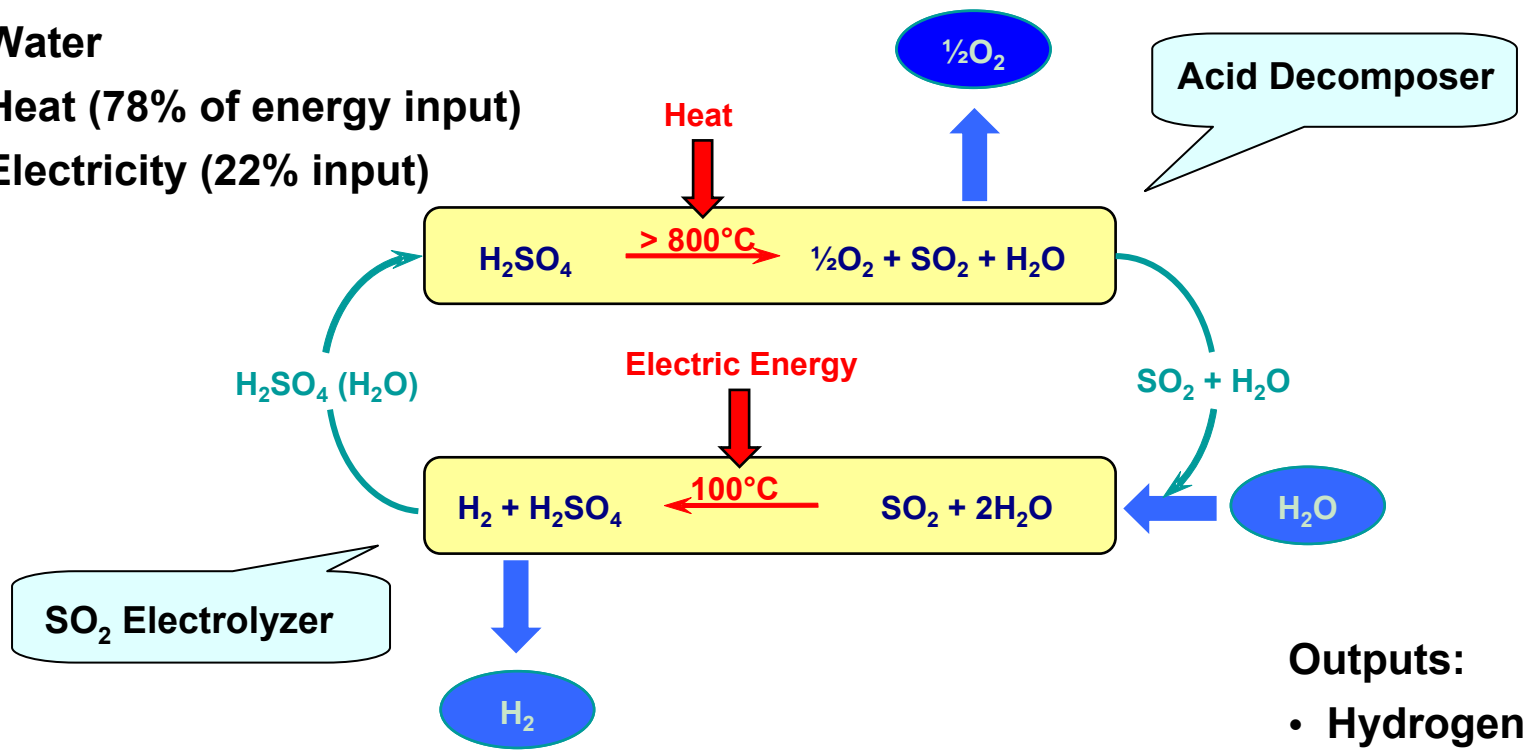
- **HyS Process Design Optimization** — *90% Complete*
  - Collaboration with Westinghouse Electric
  - Improved flowsheet and updated plant cost analysis
- **Component Characterization and Development** — *70% Complete*
  - Electrodes and electrocatalysts evaluations
  - Membrane selection, testing and analysis (with partners)
  - Assembly of single-cell membrane-electrode assemblies
- **Single-Cell Electrolyzer Testing** — *50% Complete*
  - Design, assemble and test single-cell electrolyzers
  - Temperature, pressure and acid strength effects
  - Post-test examinations and analysis
- **Multi-cell Stack** — *100% Complete*
  - Modify test facility for larger stack testing
  - Fully characterize multi-cell stack performance
  - Post-test examinations and analysis

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**

SO_2-Depolarized Anode Significantly Reduces Electricity Needed to Electrolyze Water

- **Water electrolysis half-cell reactions:**

$H_2O(l) \rightarrow ½\ O_2(g) + 2\ H^+ + 2\ e^-$	anode reaction
$2\ H^+ + 2\ e^- \rightarrow H_2(g)$	cathode reaction
$H_2O(l) \rightarrow ½\ O_2(g) + H_2(g)$	net reaction

Standard cell potential, E° = -1.229 V at 25°C

- **SO_2-depolarized electrolysis half-cell reactions:**

$2\ H_2O(l) + SO_2(aq) \rightarrow H_2SO_4(aq) + 2\ H^+ + 2\ e^-$	anode reaction
$2\ H^+ + 2\ e^- \rightarrow H_2(g)$	cathode reaction
$2\ H_2O(l) + SO_2(aq) \rightarrow H_2SO_4(aq) + H_2(g)$	net reaction

Standard cell potential, E° = -0.158 V at 25°C

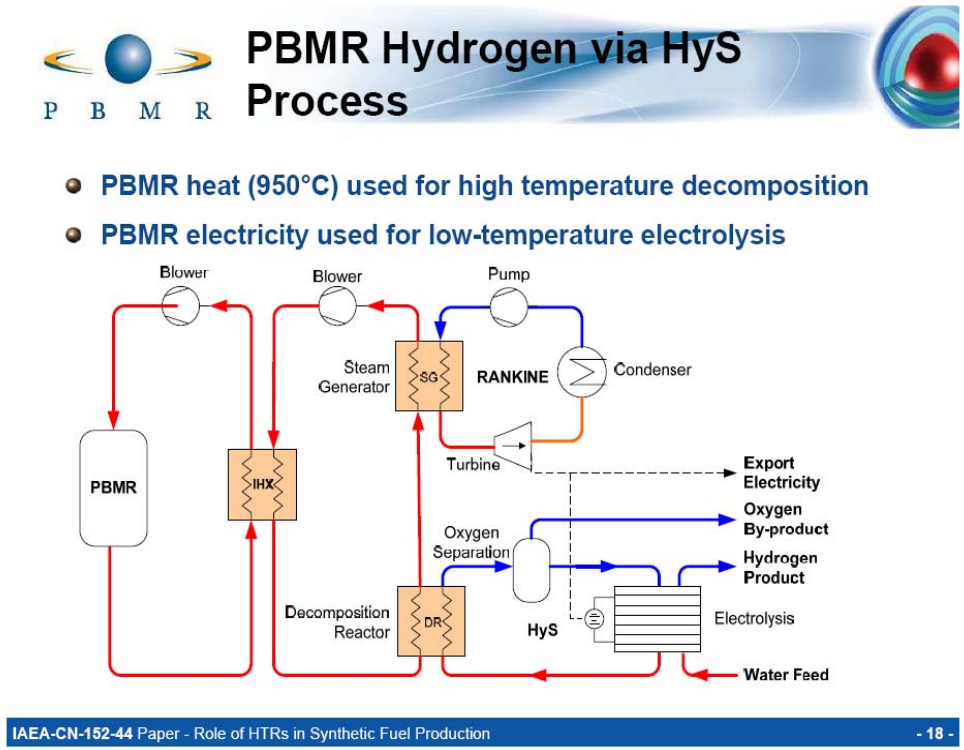
= -0.173 V in 30% H_2SO_4

= -0.262 V in 50% H_2SO_4

Improved Flowsheet Developed in Conjunction with Westinghouse Electric

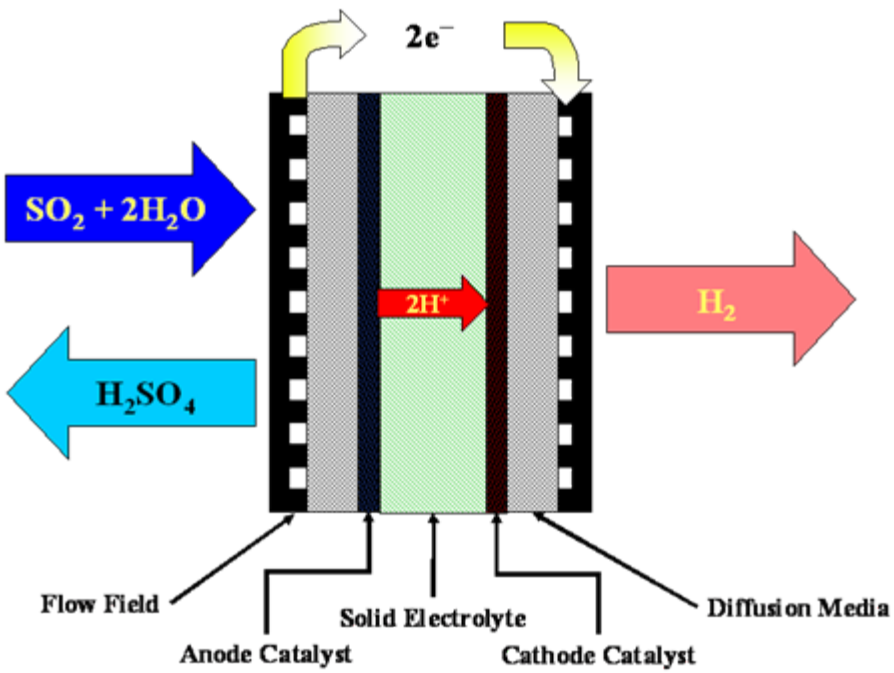
Key design improvements:

- **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%**
- **Expected to have major impact on cost of hydrogen**
- **Final equipment sizing and cost estimates in process**



Courtesy of W. Kreil, PBMR Ltd.

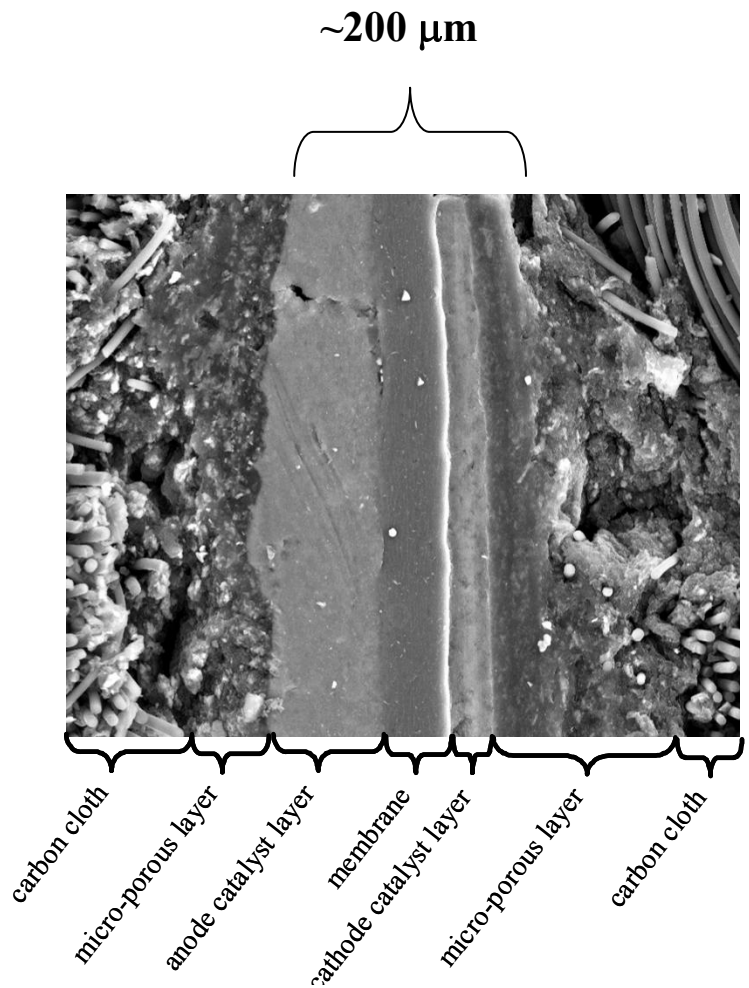
SRNL's PEM Concept for SO_2-Depolarized Electrolyzer



- SO_2 oxidized at anode to form H_2SO_4 and hydrogen ions
- Practical cell potential is 600 mV at 500 mA/cm2
- Requires efficient thermal step to regenerate SO_2 reactant
- PEM cell concept permits compact design, reduced footprint, and lower cost
- Leverages development for PEM fuel cells and water electrolyzers
- Current HyS flowsheets based on operation at 100°C and 20 bar with 50 wt% H_2SO_4

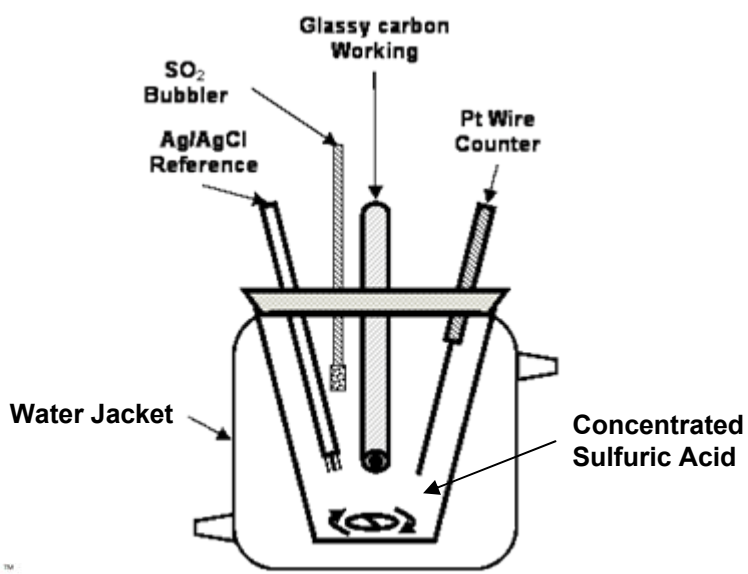
Electrolyzer Component Development Objectives

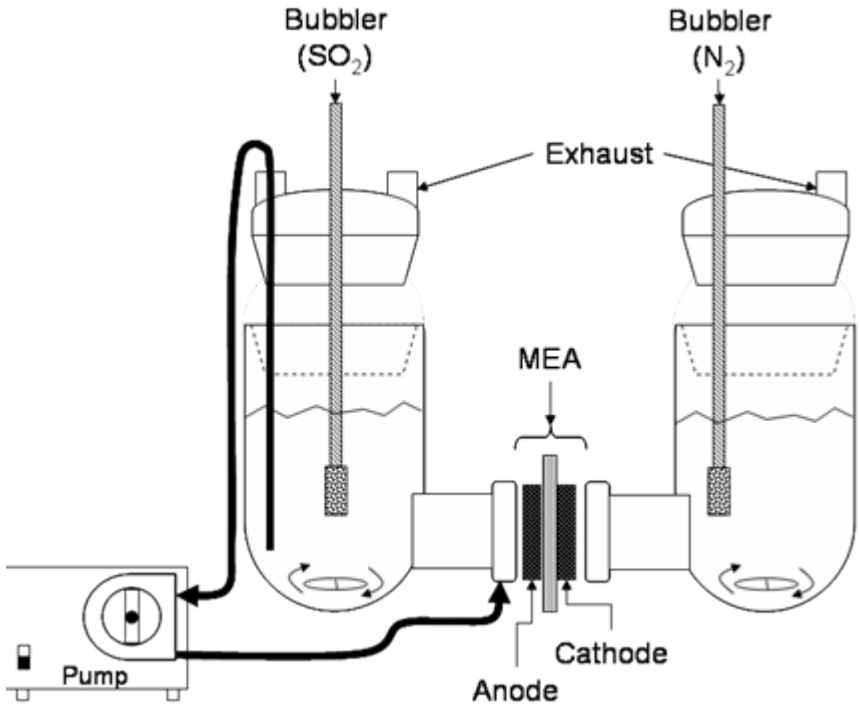
- **Proton Exchange Membrane**
  - Minimal SO_2 Transport
  - Maximum ion conductivity
- **Anode**
  - Maximum SO_2 oxidation kinetics
  - Minimal attack by SO_2/H_2SO_4
- **Cathode**
  - Maximum hydrogen formation kinetics
  - Minimal reaction with SO_2
- **Flow Field/Diffusion Media**
  - Maximize SO_2 transport to anode
  - Low pressure drop
  - Chemically and mechanically stable



Subscale Tests Used to Characterize Key Electrolyzer Components

- Glass electrolyzer unit used to measure SO2 transport thru membrane and MEA performance
- Catalyst evaluated in three electrode cell





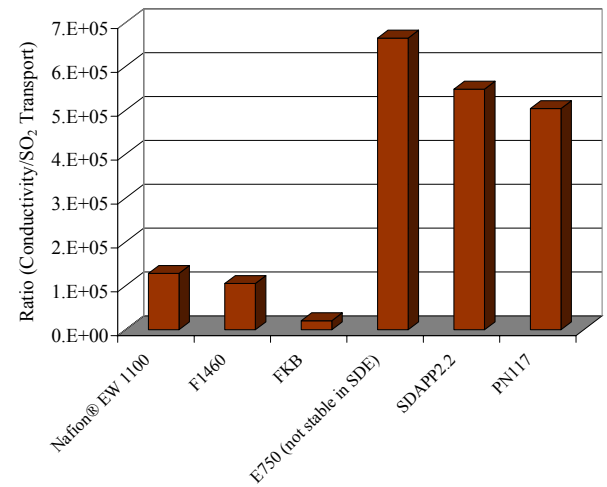
Schematic of Small-Scale (2 cm^2) Electrolyzer Test Assembly

Improved Membranes and Electrocatalysts being Developed

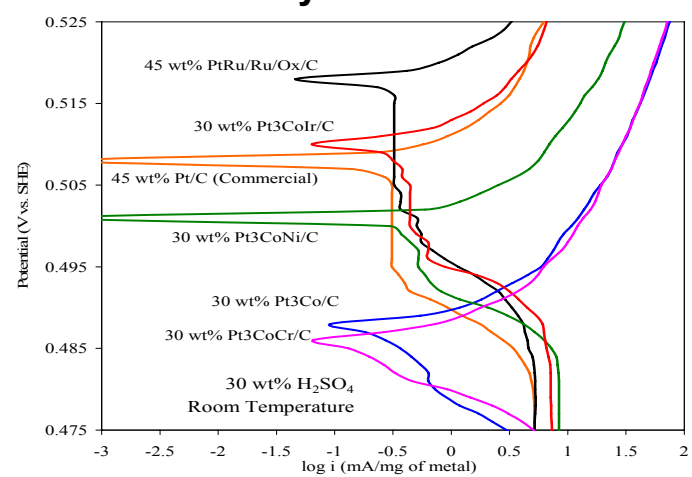
Testing has helped to characterize component performance and identify promising options

- Conventional Nafion membranes have good conductivity, but suffer from relatively high SO_2 transport
- Improvements of 5x versus Nafion achieved to date; new membranes sought with >10x
- Membranes for Direct Methanol Fuel Cells operating at higher temperatures appear attractive
- Platinum is the baseline electrocatalyst; Pt alloy catalysts show improved performance and excellent stability
- Palladium electrocatalyst rejected due to poor performance and instability

Membrane Test Results



Catalyst Evaluations

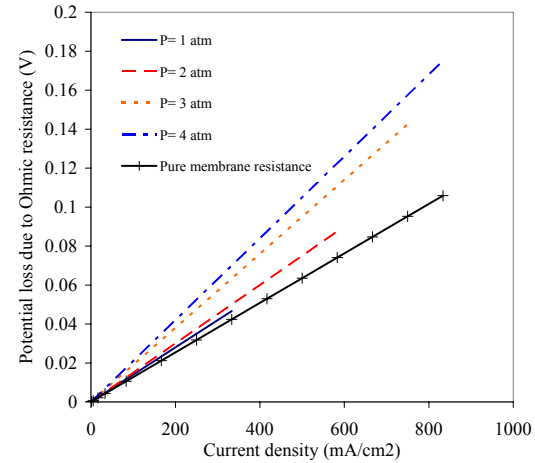


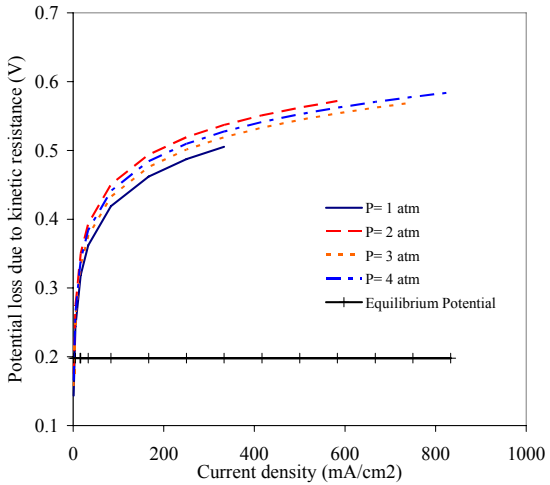
Improving Reaction Kinetics has Biggest Impact on Cell Performance

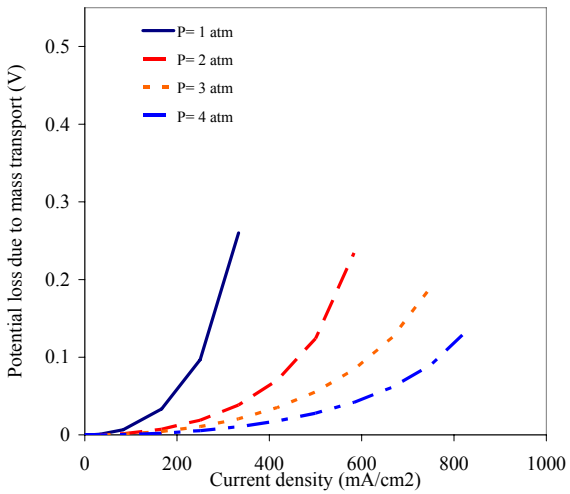
Test results fitted with empirical equation (3 atm, 80C and 500 mA/cm^2)

Kinetics	78 % of overpotential
Ohmic Losses	14 %
Concen. Polar.	8 %

Plan: Improved catalyst and higher operating temperature (100 - 120°C)

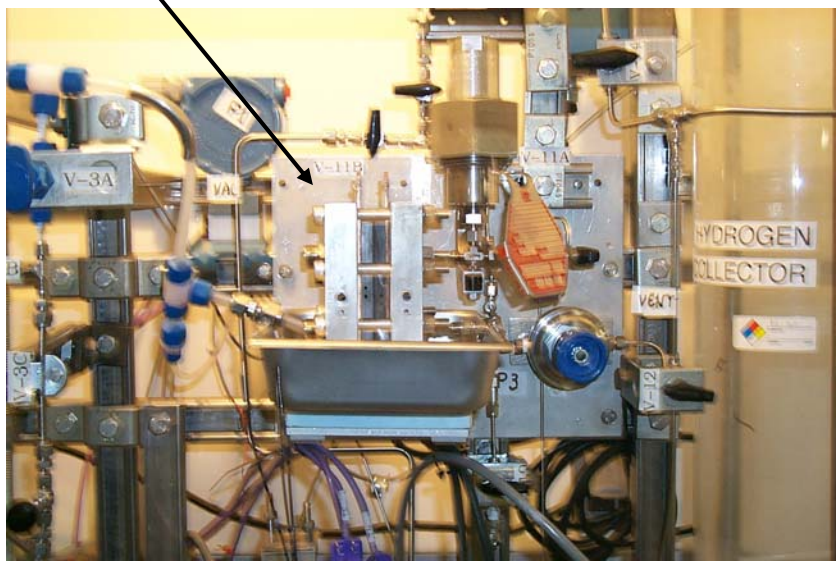






Single-cell Testing

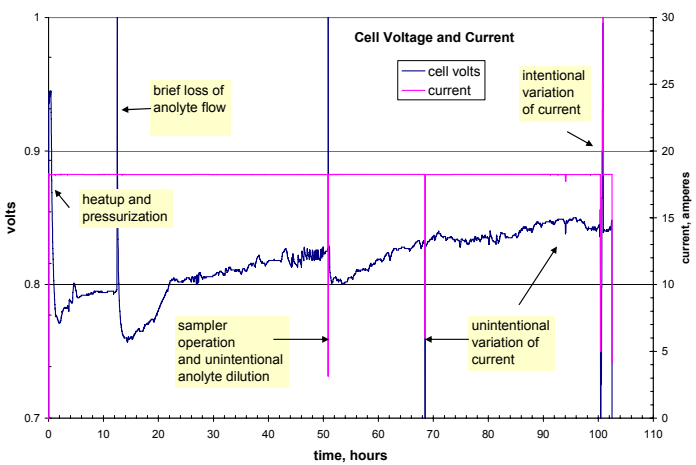
SO_2-depolarized electrolyzer



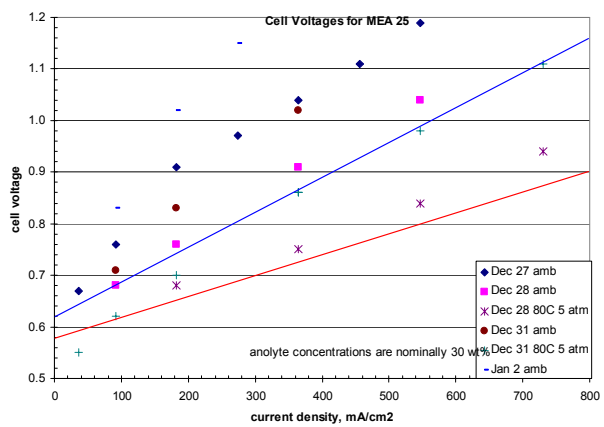
Single Cell Electrolyzer (60 cm^2 active area)

Single Cell Test Results

Twenty-six different single cell units have been tested at up to 80°C and 6 bar. 100-hour longevity test completed. Current density up to 1100 mA/cm2 vs 500 mA/cm2 goal. Voltage at design point of 760 mV vs 600 mV goal. Higher temp and pressure plus improved catalysts expected to lower voltage.



100 Hour Longevity Test



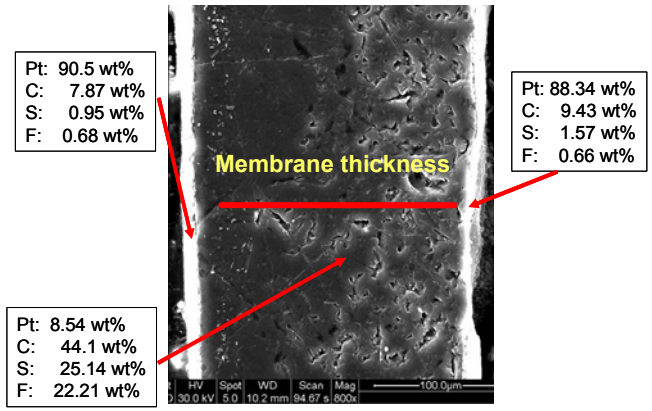
Blue line – best ambient (MEA 14)

Red line – best at T&P (MEA 19)

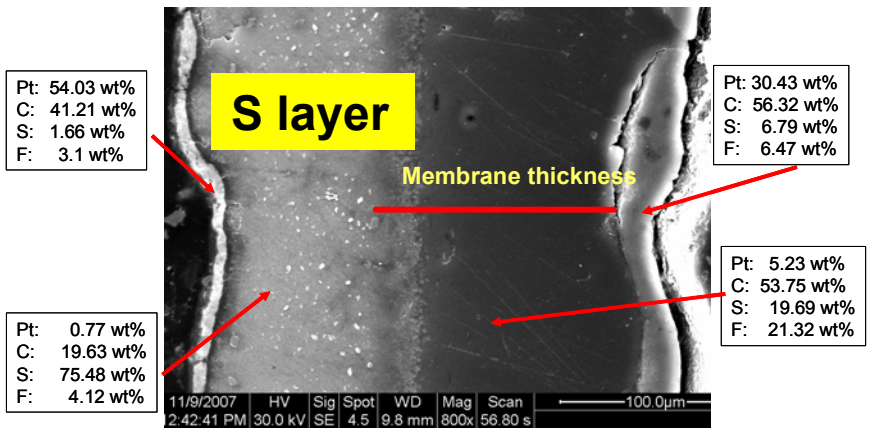
Single Cell Test Results

Reduction of Sulfur Deposition is a Key Technical Objective

- SO_2 diffuses thru PEM
- Reduction at cathode can result in S deposits
- Certain designs and operating conditions avoid deposits
- Multiple approaches
  - Modify membrane
  - Modify operating conditions
  - Alternative cell design



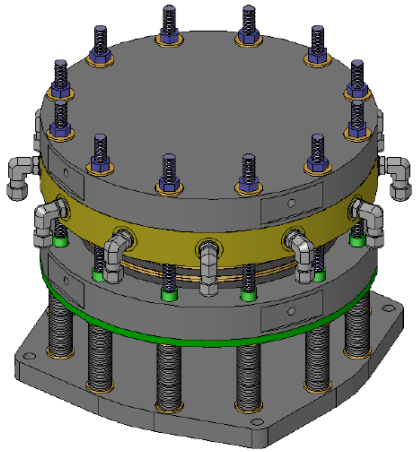
MEA 9, N117 with Pt black catalyst



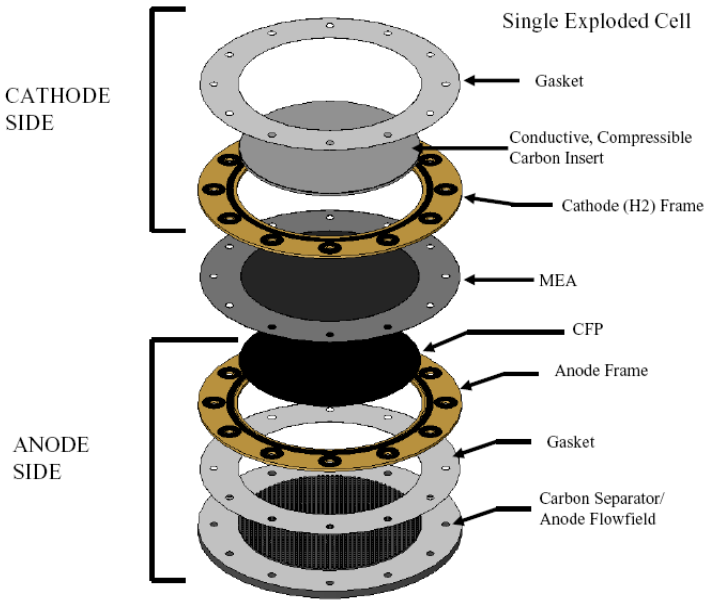
MEA 20, N115 with Pt/C catalyst

Multi-cell Stack Development

- Established partnership with Giner Electrochemical
- Leverages existing PEM water electrolyzer technology
- Maximizes use of existing components and hardware
- Incorporates SRNL experience with PEM-type SO_2 electrolysis
- Bi-polar 3-cell stack using round plates with 160 cm^2 active area per cell
- Rated capacity is 100 lph of hydrogen production under SO_2-depolarized conditions

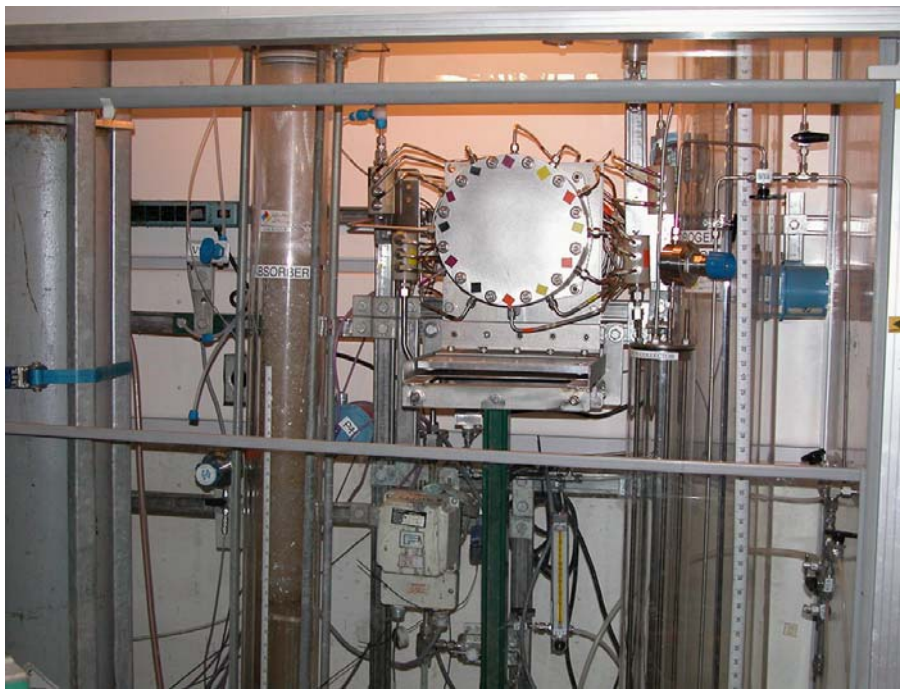


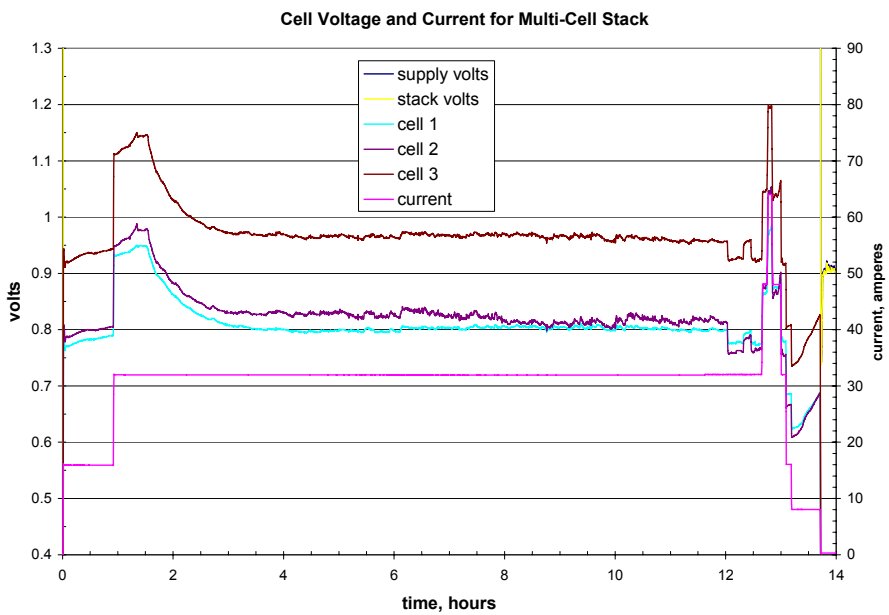
3-cell SDE



Multi-Cell Stack Testing Completed

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





Future Work

- **FY08**
  - Continue component development of improved cell membranes and electrocatalysts; select design for integrated lab-scale test
  - Characterize promising components in single cell tests
  - Verify solution to sulfur crossover issue
  - Continue work with industry, lab and university partners on alternative cell design approaches
- **FY09:**
  - Continue electrolyzer development; identify optimum membrane; extend operation to more severe conditions; scale-up to larger capacities
  - Modify test facility for higher temp operation (>100°C)
  - Run single cell tests at higher temp and for extended time (>1000 hour)
  - Design and build an Integrated Lab-Scale Experiment of HyS, including high temperature acid decomposition and SO_2/O_2 separation

Summary

- ***Relevance*** **HyS Process combined with advanced nuclear reactors (or solar receiver) can be an important hydrogen production option**
- ***Approach*** **Develop PEM-based SO_2-depolarized electrolyzer and combine with acid decomposition system from SI project. Maintain balanced program including cell development and system testing.**
- ***Technical Accomplishments*** **Key cell components defined; longevity test completed; multi-cell stack demonstrated; high efficiency HyS flowsheet completed**
- ***Technology transfer/collaborations*** **Active partnership with Westinghouse on plant design; partnership with Giner on electrolyzer manufacture; collaborations with USC, SNL and several other university partners**
- ***Future Work*** **Complete electrolyzer development and scale-up; demonstrate complete cycle in an integrated lab-scale experiment**