Hybrid Sulfur Thermochemical Process Development

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DOE Hydrogen Program
2008 Annual Merit Review

Project PD26

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.

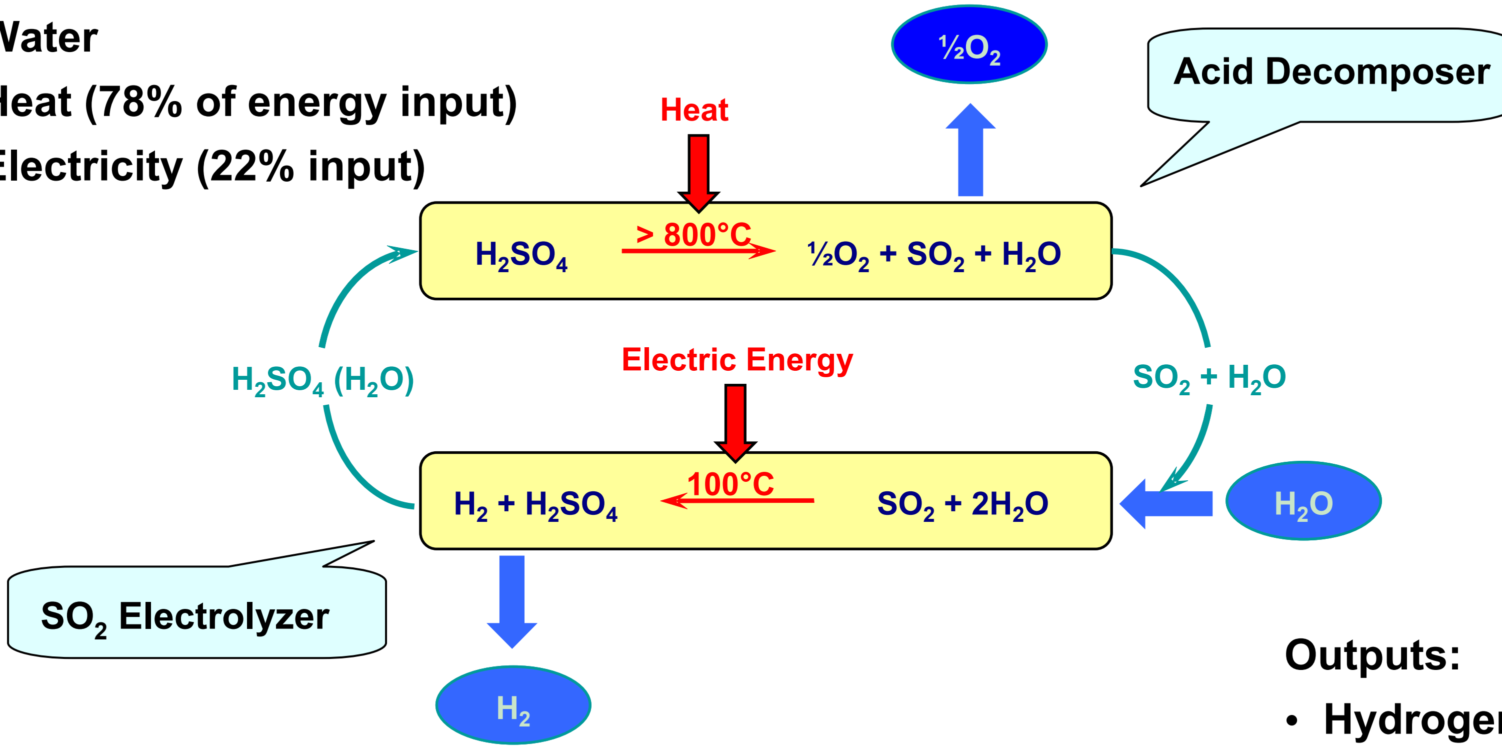
- **HyS Process Design Optimization** — *90% Complete*
  - Collaboration with Westinghouse Electric
  - Improved flowsheet and updated plant cost analysis
- **Component Characterization and Development** — *70% Complete*
  - Electrodes and electrocatalysts evaluations
  - Membrane selection, testing 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:**

$H_2O(l) \rightarrow \frac{1}{2} O_2(g) + 2 H^+ + 2 e^-$	anode reaction
$2 H^+ + 2 e^- \rightarrow H_2(g)$	cathode reaction
$H_2O(l) \rightarrow \frac{1}{2} O_2(g) + H_2(g)$	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

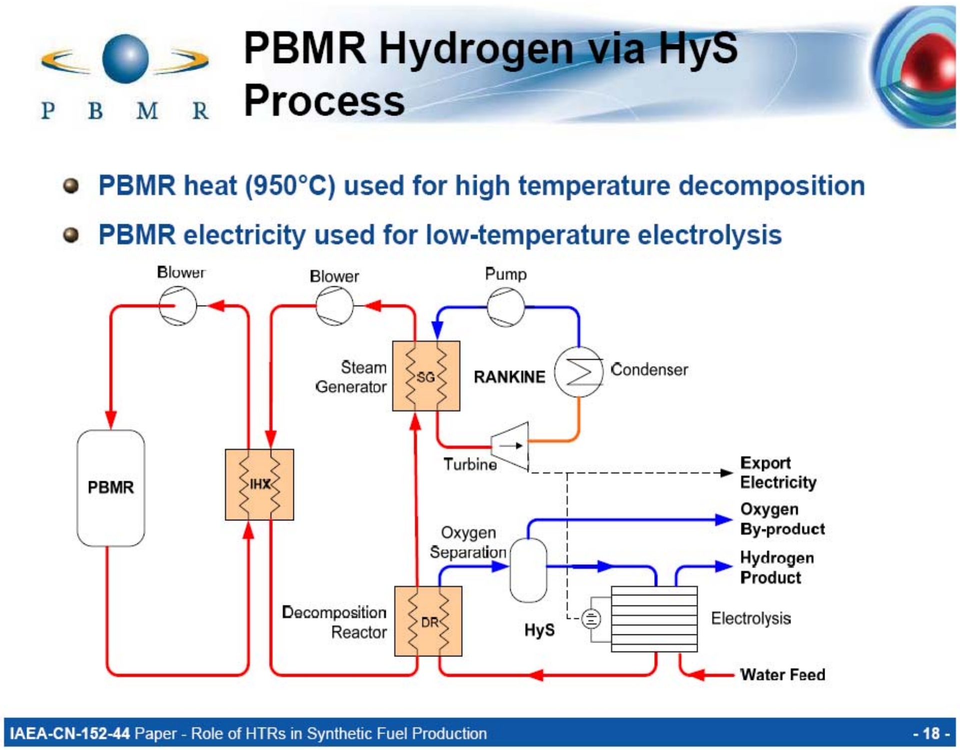
= -0.173 V in 30% H_2SO_4

= -0.262 V in 50% H_2SO_4

Improved Flowsheet Developed in Conjunction with Westinghouse Electric

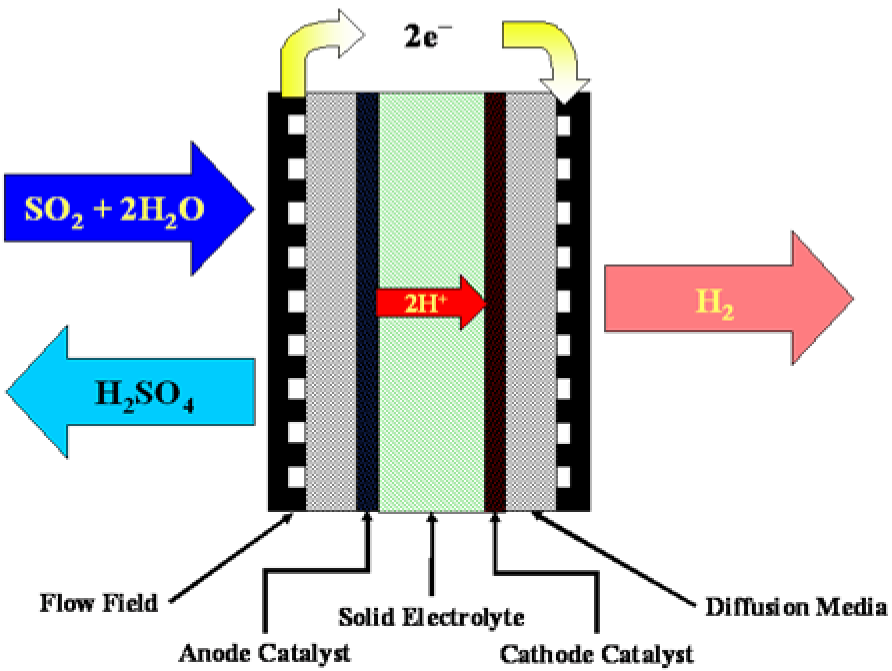
Key design improvements:

- 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.

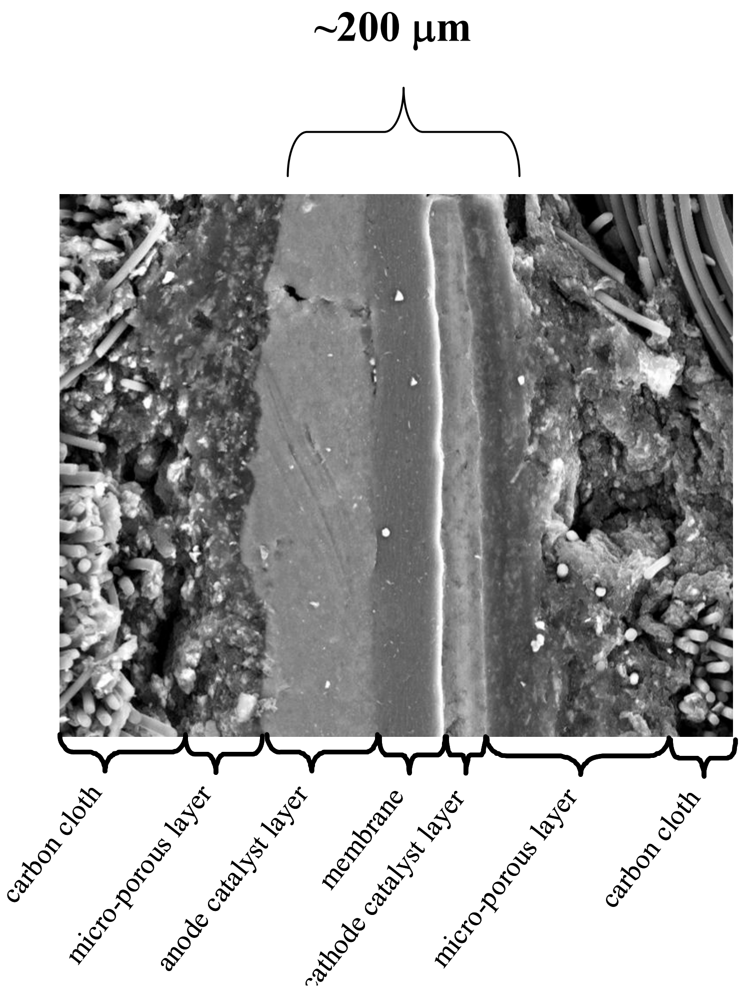
SRNL's PEM Concept for SO_2-Depolarized Electrolyzer



- 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

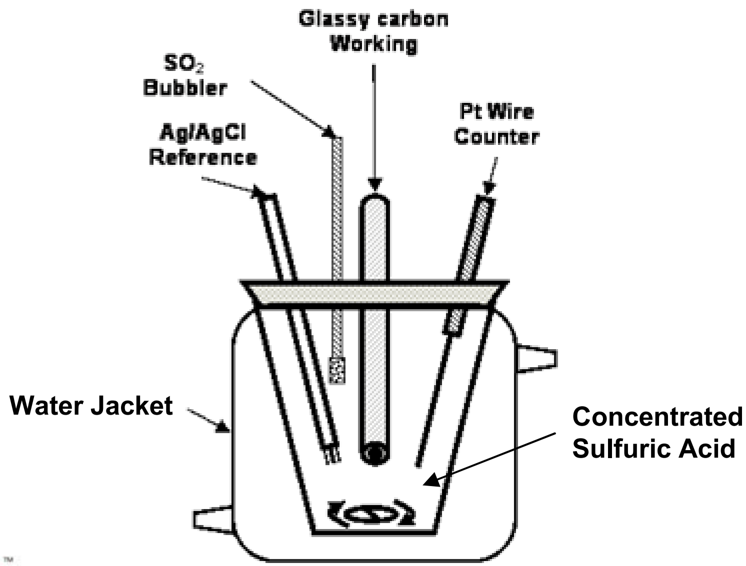
Electrolyzer Component Development Objectives

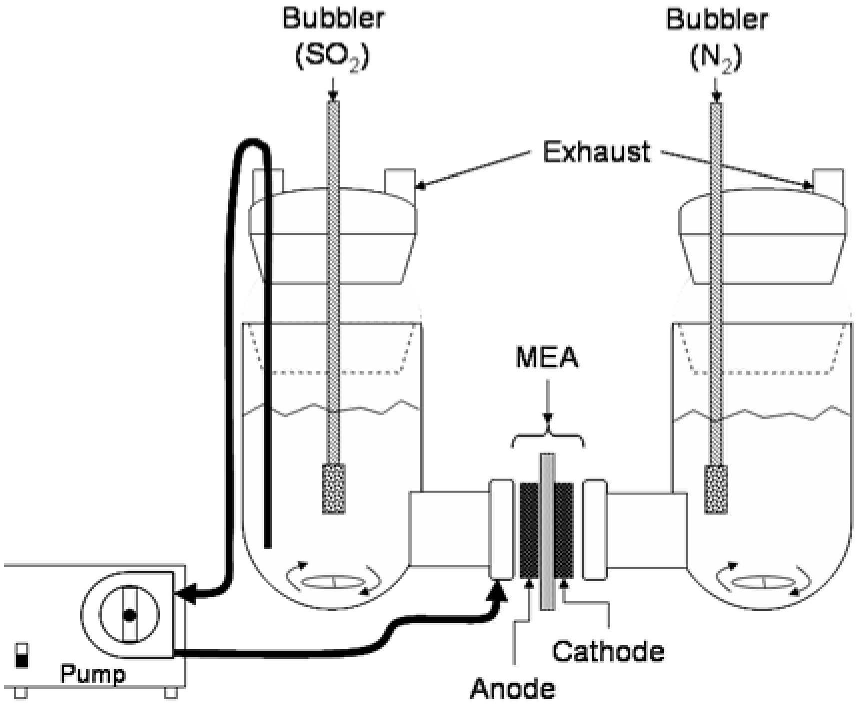
- **Proton Exchange Membrane**
  - Minimal SO_2 Transport
  - Maximum ion conductivity
- **Anode**
  - Maximum SO_2 oxidation kinetics
  - Minimal attack by SO_2/H_2SO_4
- **Cathode**
  - Maximum hydrogen formation kinetics
  - Minimal reaction with SO_2
- **Flow Field/Diffusion Media**
  - Maximize 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**





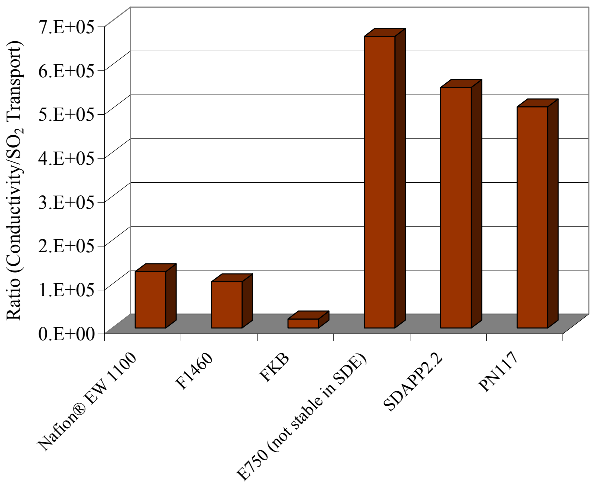
Schematic of Small-Scale (2 cm^2) Electrolyzer Test Assembly

Improved Membranes and Electrocatalysts being Developed

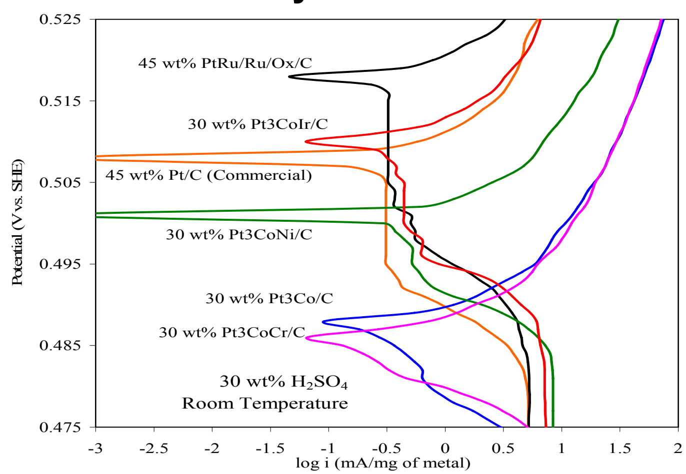
Testing has helped to characterize component performance and identify promising options

- **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

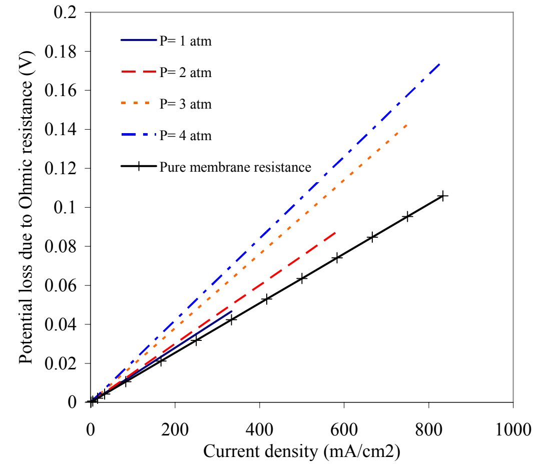


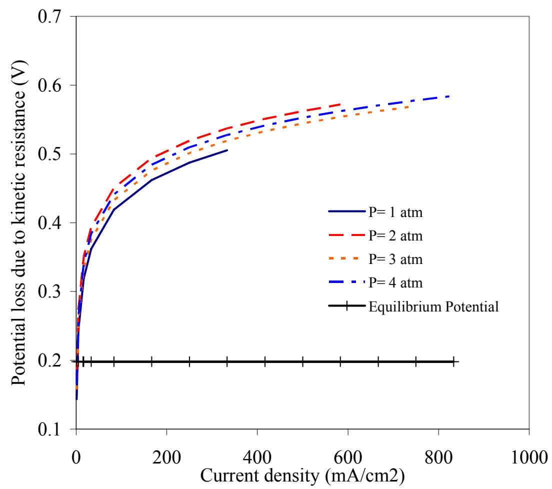
Improving Reaction Kinetics has Biggest Impact on Cell Performance

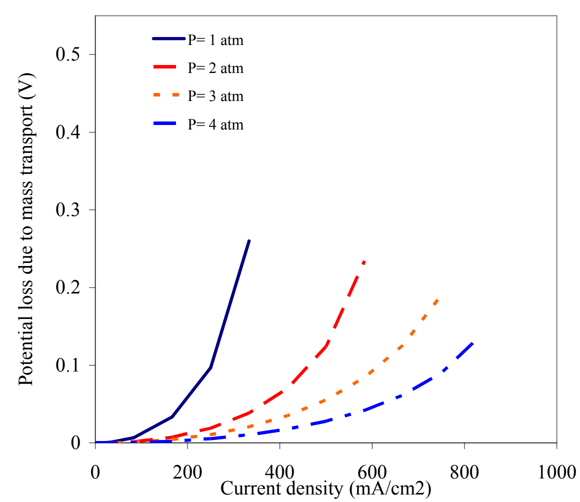
Test results fitted with empirical equation (3 atm, 80C and 500 mA/cm^2)

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

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







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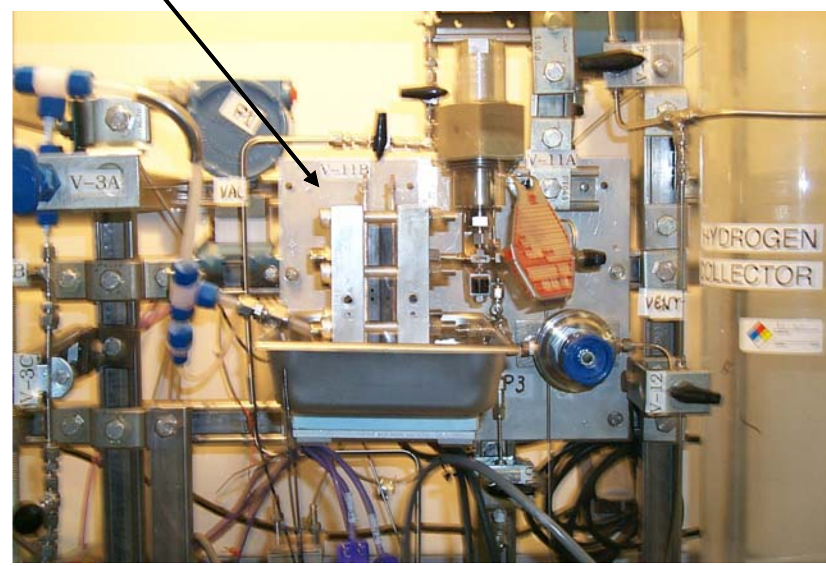
Single-cell Testing

Electrolyzer Test Facility

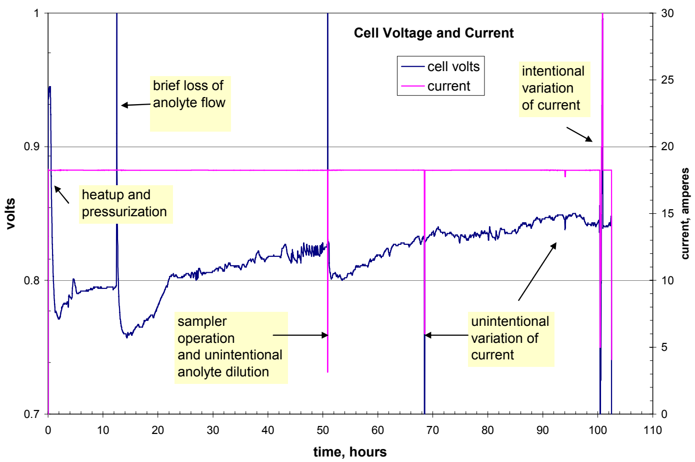
SO_2-depolarized electrolyzer



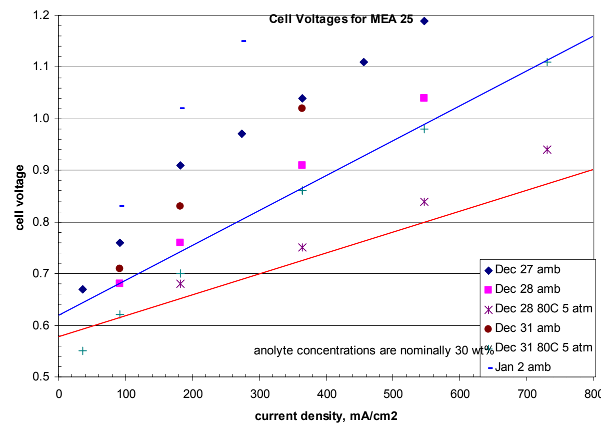
Single Cell Electrolyzer (60 cm^2 active area)

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



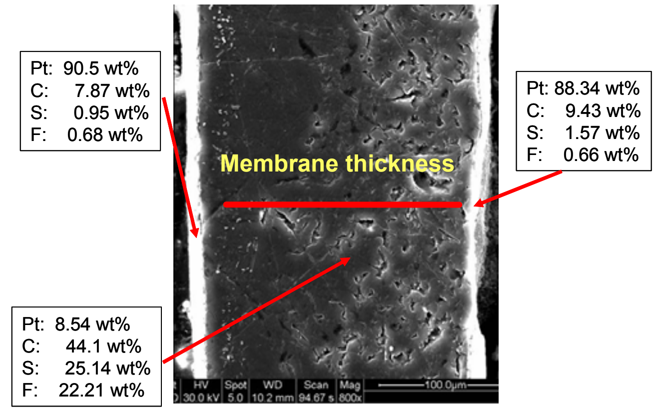
Blue line – best ambient (MEA 14)

Red line – best at T&P (MEA 19)

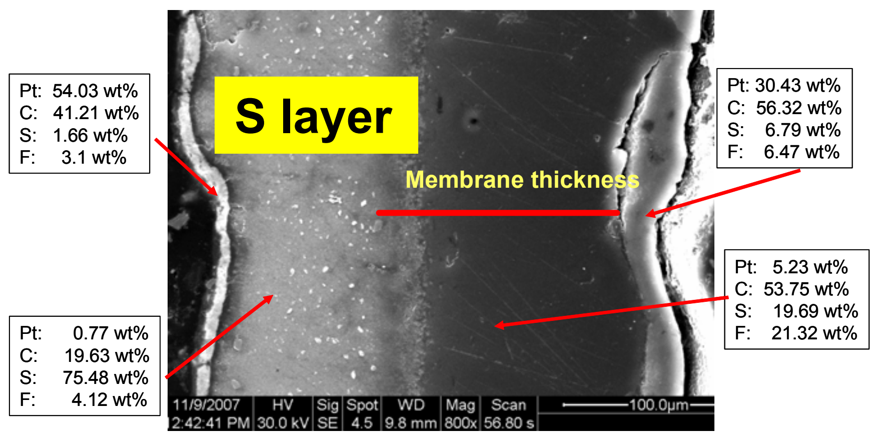
Single Cell Test Results

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



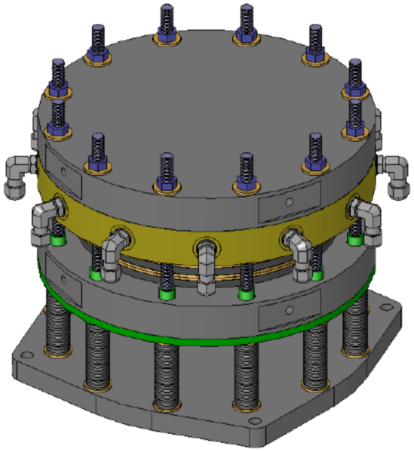
MEA 9, N117 with Pt black catalyst



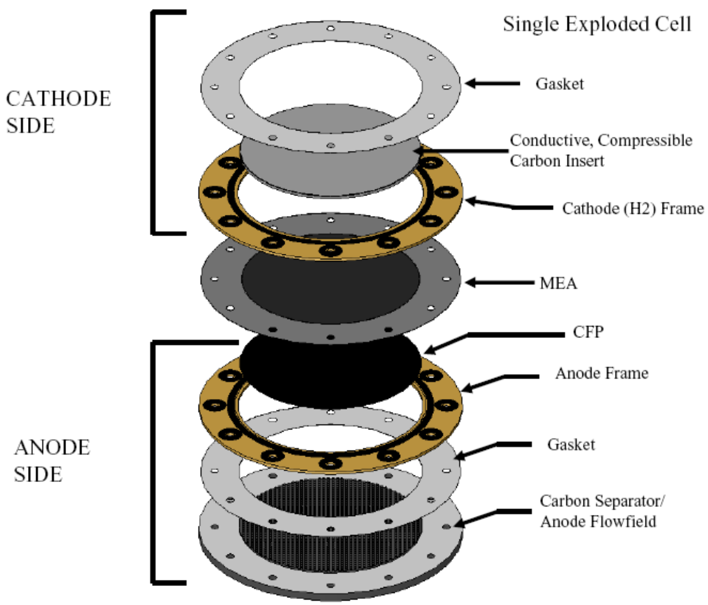
MEA 20, N115 with Pt/C catalyst

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

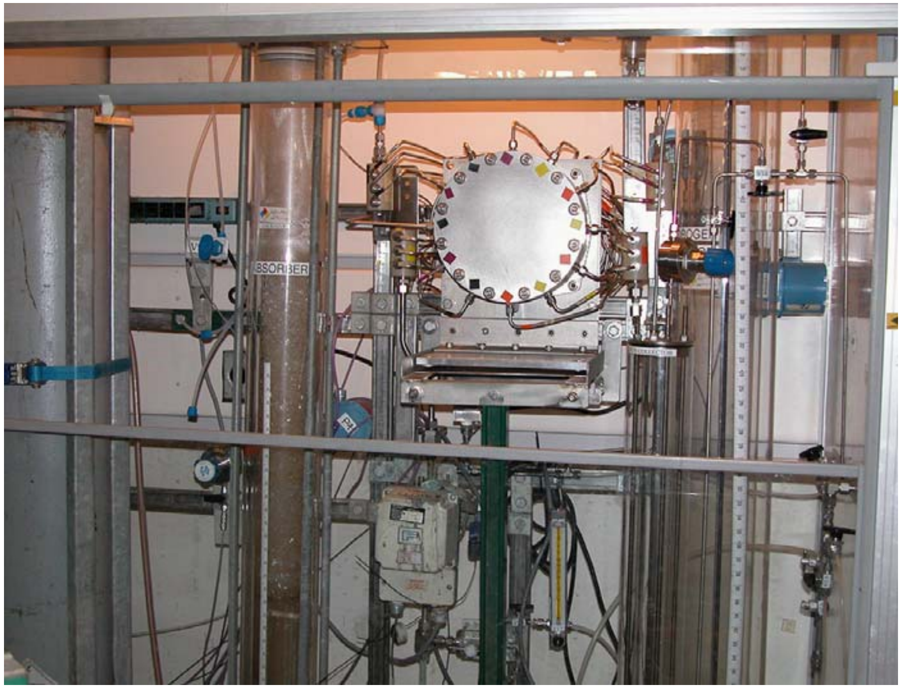


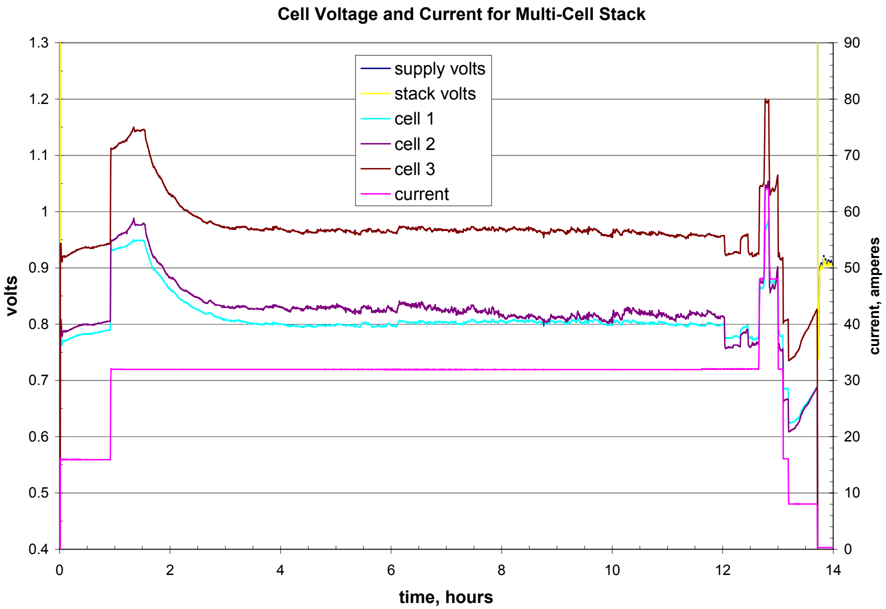
3-cell SDE



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





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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**