Hybrid Sulfur Thermochemical Process Development

William A. Summers

Savannah River National Laboratory

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Project ID # PD21

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Overview

Timeline

- Start Date: June, 2004
- End Date: Sept, 2010
- 33% Complete

Budget

- Total Project Funding
  - Total thru FY10 = TPD
  - DOE Share = 100% (to date)
- FY06 Funding = $1200 K
  - Carryover to FY07 = $274 K
- FY07 Funding = $1200 K

Barriers

- High-temperature thermochemical technology
- High temperature robust materials
- Nuclear Hydrogen production costs
- TARGET – Technical feasibility and economic viability for centralized hydrogen production from nuclear

Partners

- Giner Electrochemical
- Univ. of So. Carolina – U-NERI
- Westinghouse Electric
- Sandia National Laboratory

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Objectives

- **Overall:** Develop the Hybrid Sulfur thermochemical cycle and demonstrate in an integrated laboratory scale experiment producing >100 lph of hydrogen

- **FY06:** Develop and test an SO2 depolarized electrolyzer (SDE) using PEM-type cell design
  - Characterize, analyze and select cell components
  - Test single cell SDE electrolyzers at elevated temperature and pressure
- **FY07:** Develop improved electrolyzers; demonstrate extended operation capability; scale-up to larger size
  - Continue to identify and develop improved cell components
  - Conduct 100 hour longevity test on single cell SDE
  - Design and build multi-cell SDE with 100 lph hydrogen capacity

FY07 Plan and Approach

- **Component Selection and Characterization** — *45% Complete*
  - Electrodes and electrocatalysts
  - Membrane selection, testing and analysis
  - Assembly of single-cell membrane-electrode assemblies
- **Single-Cell Characterization Testing** — *85% Complete*
  - Upgrade test facility (instrumentation, 80°C, 6 bar)
  - Design, assemble and test single-cell electrolyzers
  - Cell flow and mass transfer optimization
  - Temperature, pressure and acid strength effects
- **Longevity Testing** — *35% Complete*
  - 100-hour test on promising single cell electrolyzer
- **Multi-cell Stack** — *50% Complete*
  - Design and construct multi-cell SDE for >100 lph H2 production
  - Collaborate with industrial PEM electrolyzer company
- **Critical thermophysical properties** — *20% Complete*
  - Determine properties for $H_2O/SO_2/H_2SO_4$ mixtures

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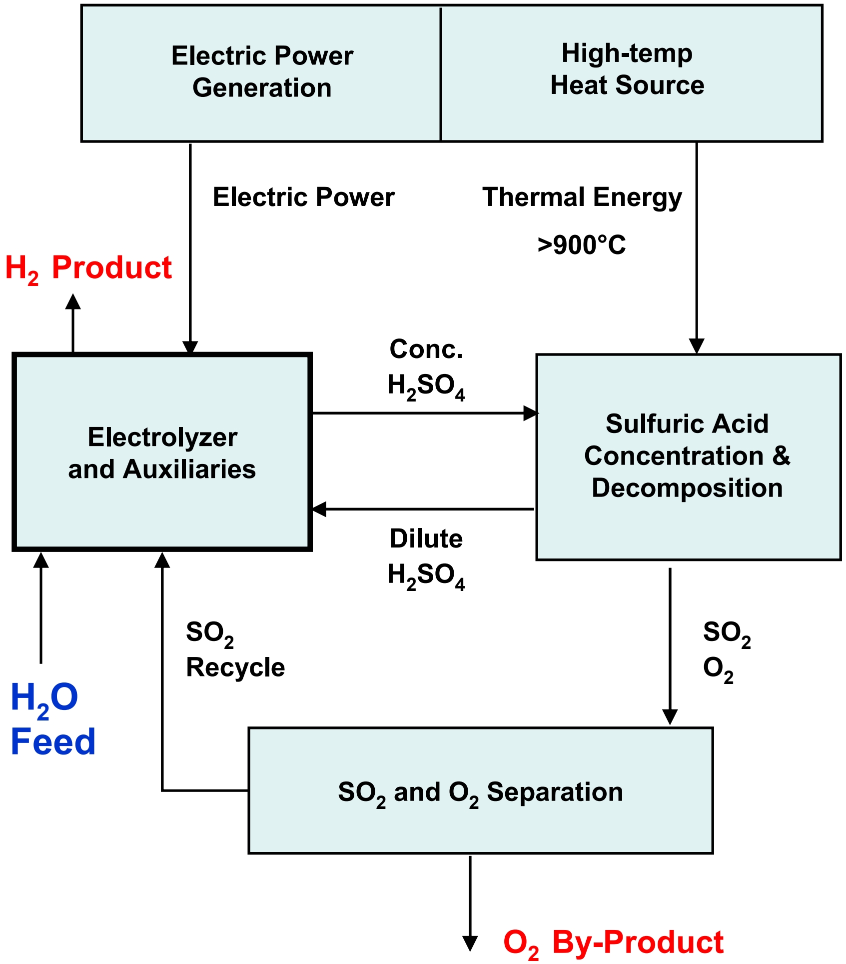
Accomplishments Summary

- **Process Design Updated**
  - Improved system design with higher process efficiency of >54% (HHV)
- **Key SDE Components Selected and Characterized**
  - Nafion 115 and hydrocarbon (SDAPP) membranes most promising
  - Pt/C selected for anode and cathode electrocatalyst
- **Extensive Single Cell Electrolyzer Tests Completed**
  - Eleven PEM-based SO_2-depolarized electrolyzers (SDE) tested
  - SDEs characterized at up to 80°C, 6 atm, 30-50 wt% sulfuric acid
  - Preparation completed for 100 hour longevity testing
- **Larger Multi-cell Stack in Progress**
  - Partnership with Giner Electrochemical established
  - 3-cell, 100 lph stack design nearing completion
  - Multi-cell electrolyzer completion scheduled for September, 2007

Hybrid Sulfur Thermochemical Process

- **Simplest thermochemical cycle**
- **Requires electric & thermal input**
- **High temperature (>900°C) heat source could be nuclear reactor or solar thermal**
- **Thermochemical system has three main processing units**
  - Sulfuric Acid concentration and decomposition
  - SO_2/O_2 separation
  - SO_2-depolarized electrolyzers

Development Focus



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HyS Chemical Reactions

Hybrid Sulfur Chemistry

$H_2SO_4 \leftrightarrow H_2O + SO_2 + ½O_2$
(thermochemical; 800-900 °C)

$SO_2 + 2\ H_2O \rightarrow H_2SO_4 + H_2$
(electrochemical; 80-120 °C)

Net Reaction: $H_2O \rightarrow H_2 + ½O_2$

Sulfur Dioxide Depolarized Electrolyzer (SDE)

Anode Reaction:

$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$ $E_o = -0.158$ V

Cathode Reaction:

$2H^+ + 2e^- \rightarrow H_2$ $E_o = 0.000$ V

Net Reaction:

$\mathbf{SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2}$ $\mathbf{E_o = -0.158\ V}$

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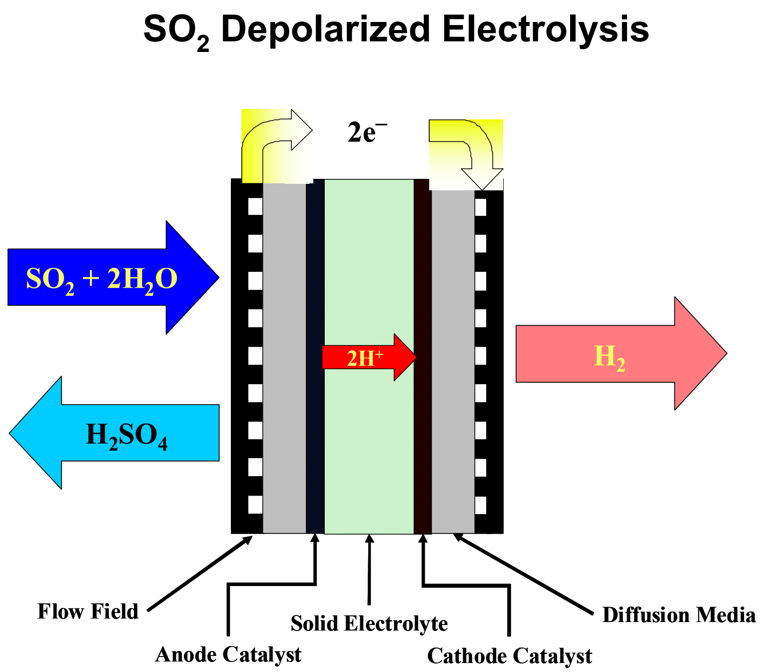
HyS Electrolyzer Concept

- Sulfur dioxide is oxidized at the anode to form sulfuric acid
- Reversible cell voltage to split water reduced from 1.23 to 0.158 volts per cell
- Practical cell voltages 0.5 – 0.6 volts (~75% less than direct electrolysis)
- PEM cell design permits compact design, reduced footprint and lower cost
- Economics dictate design with high current density and low per cell voltage
- Current HyS plant design based on electrolyzer operation at 80-120 °C and 20 bar with 50-60 wt% sulfuric acid



HyS Process History

▪ Patent for "Sulfur Cycle" issued to Westinghouse Electric Corporation	1975
▪ Two-compartment Diaphragm Cell Built	1977
▪ Closed-loop Process Demonstration by (W)	1978
▪ Solar-driven Process Design Completed by (W)	1983
▪ Development "Hiatus"	1984-2003
▪ New Process Design work by (W)	2004
▪ Conceptual Design of HyS by SRNL	2005
▪ Proof-of-Concept for PEM-based SDE	2005
▪ Pressurized, Elevated Temperature SDE Testing	2006
▪ Improved PEM Design; Multi-cell stack SDE	2007

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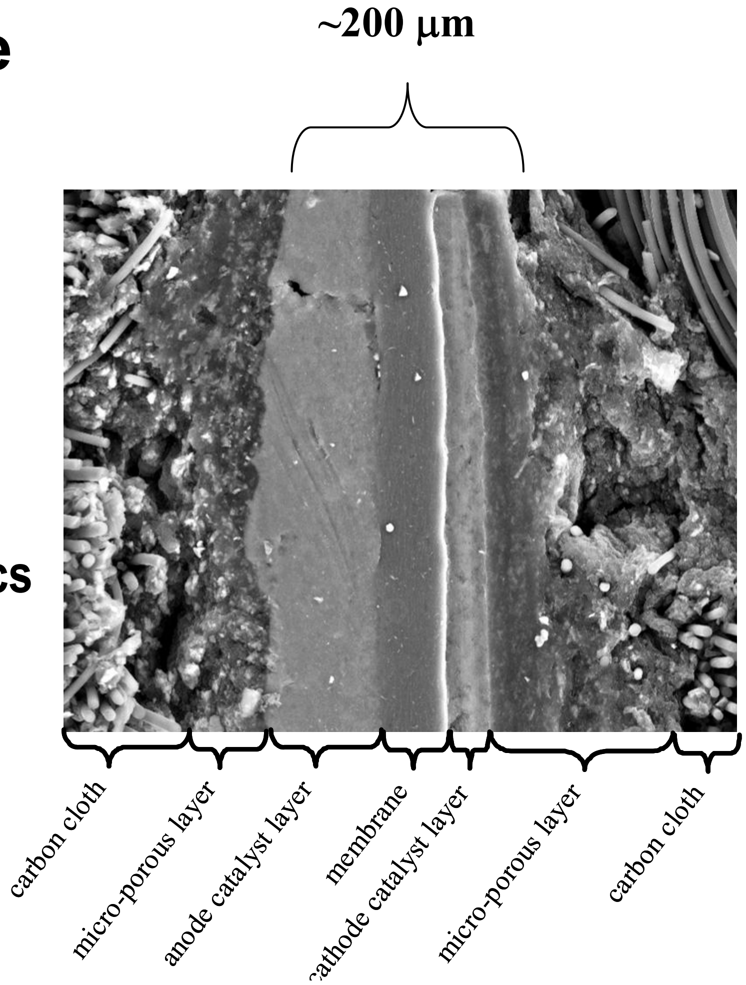
SO_2 Electrolyzer Components

- **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
  - Mininal reaction with SO_2
- **Flow Field/Diffusion Media**
  - Maximize SO_2 transport to anode
  - Low pressure drop



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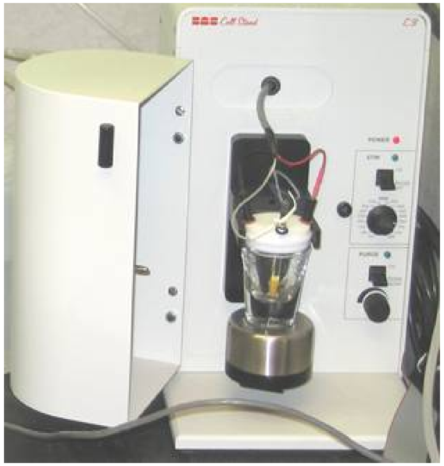
Component Development

- **Develop optimum components for sulfur dioxide-depolarized electrolyzer**
  - anode
  - cathode
  - membrane
  - flow field and diffusion media

- **Fabricate membrane electrode assemblies (MEA) for electrolyzer system testing in single-cell test facility**

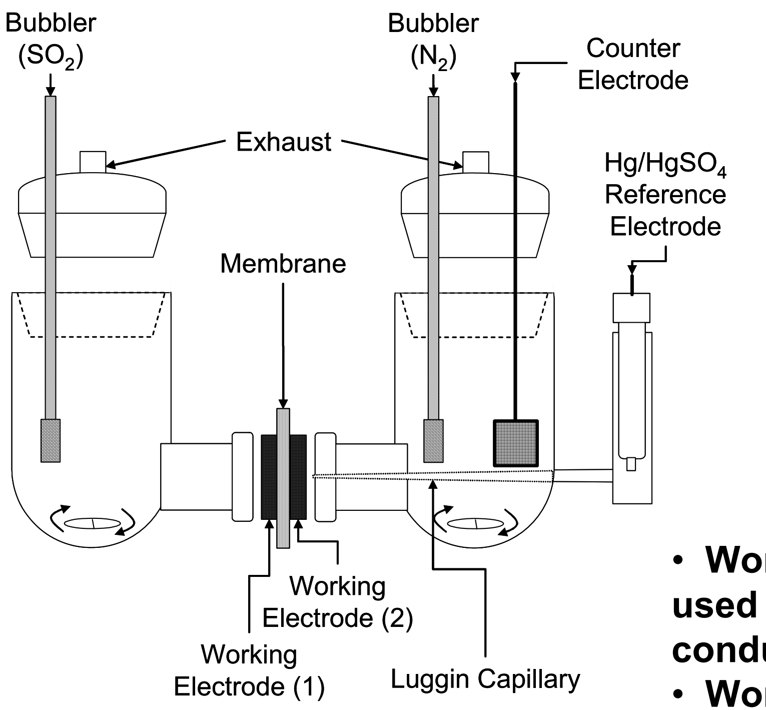
Ionic conductivity and SO2 transport test apparatus



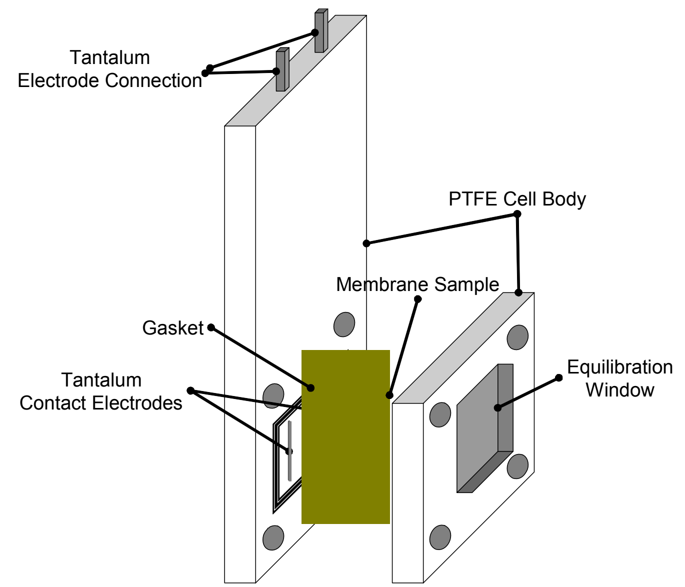
Catalyst Characterization Set-up

Membrane Characterization Set-up

Ionic conductivity and SO2 Transport Apparatus



- **Working electrode (1) is used during the ionic conductivity measurements**
- **Working electrode (2) is used during the SO2 transport measurements**



Simplified schematic of the Ionic Conductivity cell using Electrochemical Impedance Spectroscopy (EIS)

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Commercial and Experimental Membranes Characterized to Date

ID	Manufacturer	Classification	Thickness μm	Equivalent Weight g/eq
N112	DuPont	PFSA	50	1100
N115	DuPont	PFSA	130	1100
N117	DuPont	PFSA	180	1100
F-1460	Fumatech	PFSA	60	1400
F-1050	Fumatech	PFSA	50	1000
F-960	Fumatech	PFSA	60	900
Celtec-V	PEMEAS	PBI with immobilized electrolyte	100	----
Celtec-L	PEMEAS	PBI	100	----
OXPEKK	OPM	SPEKK	25	N/A
FKB	Fumatech	PEEK	80	----
E-750	Fumatech	SPEK	50	700
N-324	DuPont	Fabric Reinforced PFSA	~320	N/A
PN117	GES	Pt-treated PFSA	180	1100
SDAPP2.2	SNL	SDAPP	50	N/A
SDAPP1t	SNL	SDAPP	50	N/A
SDAPP4t	SNL	SDAPP	25	N/A
SDAPP1.6	SNL	SDAPP	76	N/A

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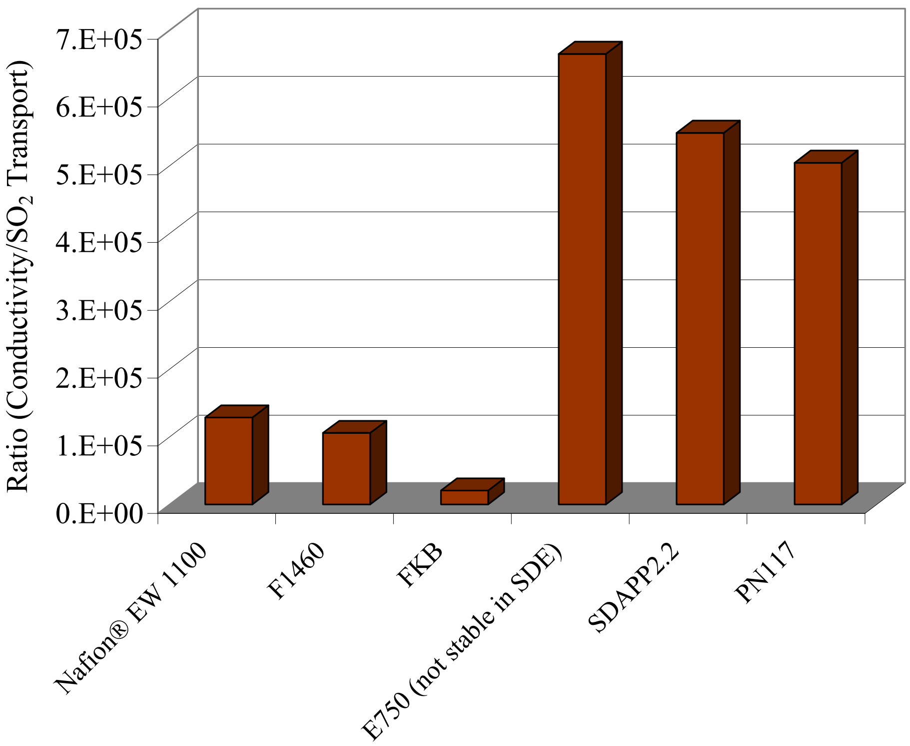
Membrane Test Results

- **High proton conductivity and low SO2 crossover are preferred**
- **E750 (SPEK polymer) has highest ratio, but it is unstable under electrolyzer conditions**
- **SDAPP (from Sandia NL) and PN117 (Pt-treated PFSA from Giner) appear promising**
- **Conventional Nafion membranes have good conductivity, but suffer from higher SO2 transport**



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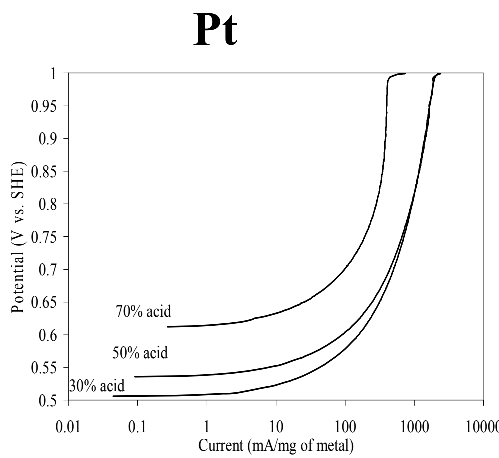
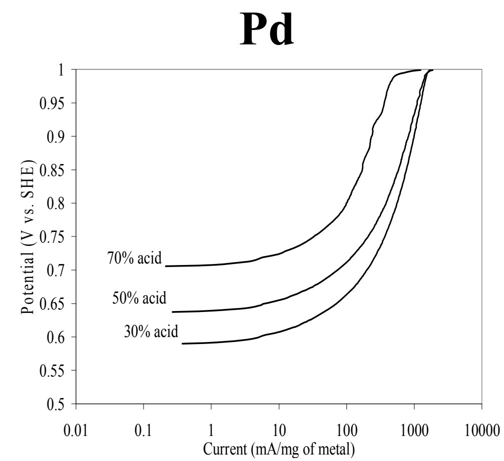
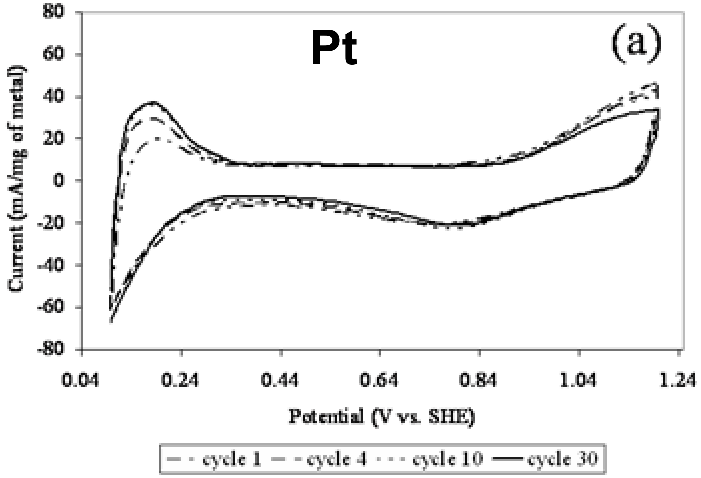
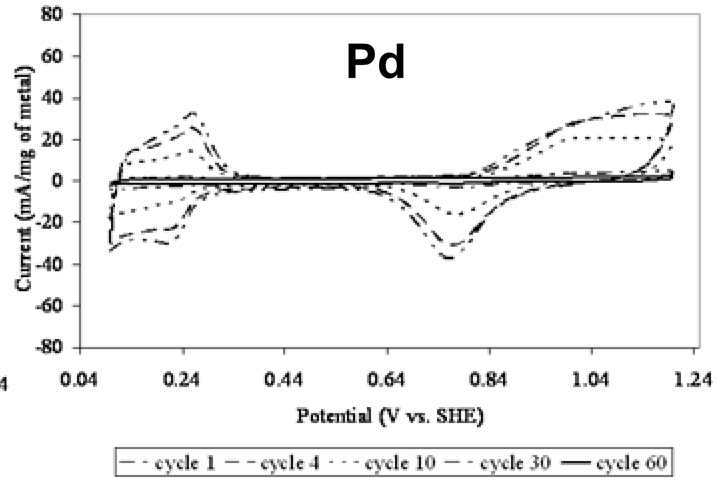
Catalyst Testing: Reaction Kinetics and Stability during Cycling

- Kinetic activity decreases as the acid strength increases
- Pt exhibits approximately 100 mV better performance than Pd
- Based on cyclic voltammetry, Pt exhibits greater stability than Pd
- Current electrocatalyst selection is Pt
- We are also studying alloy catalysts with Pt and transition metals









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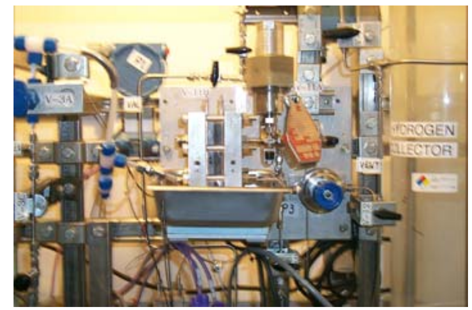
Single-cell Testing

Electrolyzer Test Facility

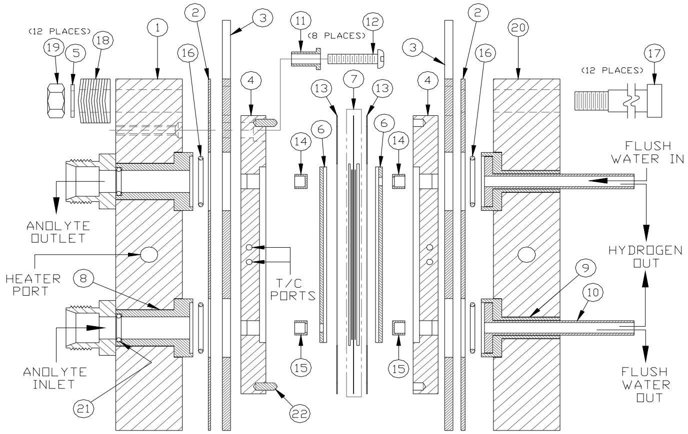
SO2-depolarized electrolyzer

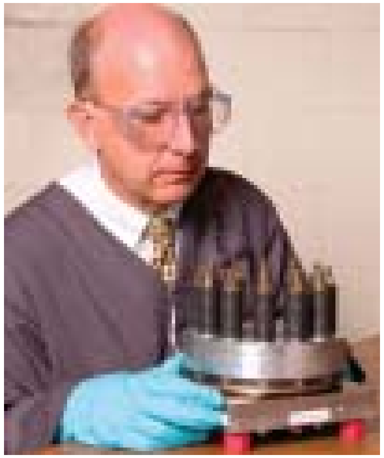


Single-cell Electrolyzer Design Variables

- MEAs with different membrane types
- MEA preparation procedures
  - Catalyst coated electrode
  - Catalyst coated membrane
  - Combined approach
- Catalyst loading
- Flowfield design
- Diffusion media
  - Carbon papers
  - Carbon cloths
  - Different micro-porous layers

SRNL Single-cell Test Electrolyzer





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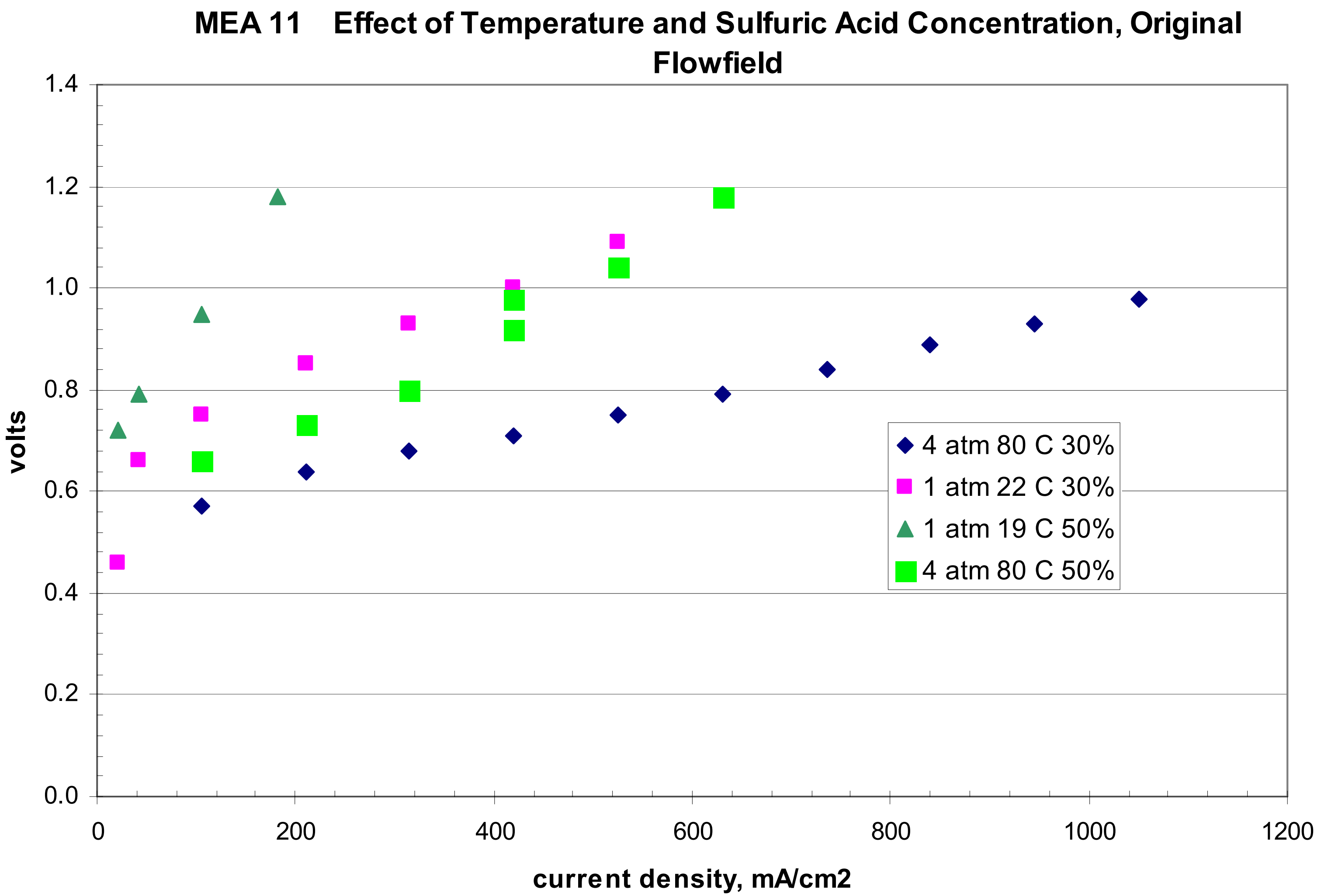
Cell Configurations Tested to Date

MEA No.	Nominal Active Cell Area, cm2	Membrane Type	Thickness (μm)	Anode Loading (mg of Pt/cm^2)	Cathode Loading (mg of Pt/cm^2)
1	50	Nafion® 115	130	0.68	0.65
2	50	Nafion® 117	180	1.1	1.1
3	50	Nafion® 117	180	1.4	1.3
4	50	Nafion® 117	180	0.9	1.0
5	50	Celtec-L	100	1.0	1.2
6	50	2 x Celtec-L	200	2.2	1.5
7	50	Celtec-V	100	0.8	0.8
8	60	Nafion® 115	130	0.8	0.6
9	60	Nafion® 117 (Giner MEA)	180	4 (Pt Black)	4 (Pt Black)
10	60	Nafion® 117 (Giner MEA)	180	1 (Pt Black)	1 (Pt Black)
11	50	Nafion® 115	130	1.09	0.72

All MEA's fabricated by SRNL unless noted. MEA #1 is catalyst-coated electrode; all others are catalyst-coated membrane. Anode/cathode electrode support: Carbon paper/carbon cloth (except MEA #1).

Performance Improves with Temperature and Declines with Acid Strength



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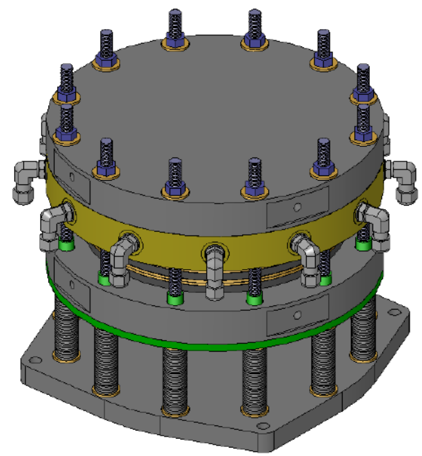
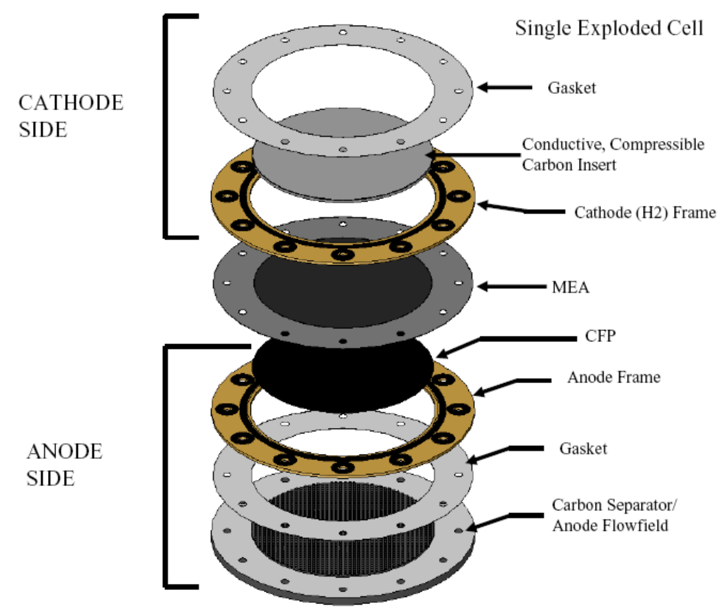
Multi-cell Stack Development

- Established partnership with Giner Electrochemical
- Leverage existing PEM water electrolyzer technology
- Maximize use of existing components and hardware
- Design in progress; stack due in September, 2007
- Bi-polar 3-cell stack using round plates with 160 cm2 active area per cell
- Rated capacity is 100 lph of hydrogen production under SO2-depolarized conditions



SDE Design



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Results and Issues

- Significant progress in cell performance has been achieved, but further improvements are required

  Status: 750 mV vs. 600 mV goal at 500 mA/cm2
- Operation at higher acid strengths, increased temperature and pressure and higher SO_2 utilization rates are required
- Longevity testing will help establish lifetime issues and material concerns
- Crossover of SO_2 and formation of elemental sulfur is a major challenge – both improved membranes and cell design and operating changes are being pursued
- Scale-up to both larger cell sizes (active area per cell) and larger stacks are required
- Leveraging of existing PEM technology and existing water electrolyzer design experience is being incorporated

Milestone Status

No.	Description	Due	Status
1	Complete single-cell test system develop.	1/15/07	Complete
2	Complete membrane selection for longevity	4/15/07	Complete
3	Complete 100-hour Longevity Test	6/15/07	On schedule
4	Complete multi-cell stack design	7/1/07	On schedule
5	Complete H2O/SO2/H2SO4 properties determination	8/1/07	On schedule
6	Complete cell component characterizations	8/15/07	On schedule
7	Complete construction of multi-cell stack	9/15/07	On schedule

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Future Work

- Continue component characterization and development of improved cell membranes
- Complete 100 hour longevity test (Level 1 Milestone)
- Complete design and construction of multi-cell stack
- Continue work with industry partners on improved membrane using innovative design approaches
- FY08:
  - Continue electrolyzer development; identify optimum membrane; extend operation to more severe conditions; scale-up to larger capacities
  - Design and build an Integrated Lab-Scale Experiment of HyS, including high temperature acid decomposition and SO_2/O_2 separation

Summary

- **SO_2 Depolarized Electrolyzer (SDE) is the key component for the success of the HyS thermochemical cycle**
- **SRNL has demonstrated the use of PEM cell technology for SDE – leading to more efficient and lower cost electrolyzer possibilities**
- **Ongoing tests will establish key cell design parameters, including membrane performance**
- **An integrated lab-scale experiment of the entire HyS Process is the next key step**
- **Successful cell development could lead to commercialization of thermochemical hydrogen production using nuclear or solar heat sources**