Hybrid Sulfur Thermochemical Process Development

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This presentation does not contain any proprietary or confidential information

Project ID # PDP 25

Overview

Timeline

- Start Date: June, 2004
- End Date: Sept, 2008
  - Complete Integrated lab-scale testing
- 25% Complete

Barriers

- High-temperature thermochemical technology
  - High performance membrane
  - Electrolyzer scale-up and cost
- High temperature robust materials
- Proof-of-concept to meet MW-scale pilot plant decision by end of FY08

Budget

- Total Project Funding – TBD
  - DOE Share = 100%
- FY05 Funding - $300 K
- FY06 - $800 K

Partners

- Univ. of So. Carolina - Electrolyzer
- Westinghouse Electric – consultation on process design
- Sandia Nat. Lab – Membranes; H_2SO_4 decomposition system development

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Objectives

- **Overall:** Develop the Hybrid Sulfur thermochemical cycle and demonstrate in an integrated laboratory scale test system producing 100 lph hydrogen
- **FY06:** Develop and test an SO_2 depolarized electrolyzer (SDE) using PEM-type cell design
  - Characterize, analyze and select cell components, including membrane, MEA, and cell flow plates
  - Test three or more single cell electrolyzers using SO_2 depolarization with sulfuric acid at up to 80°C and 6 bar

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FY06 Approach

- **Task 1 - Electrolyzer Component Selection, Analysis, and Characterization**

  35% Complete

  – Cell Membrane selection, testing and analysis
  – Anode/cathode development and electrocatalyst evaluations
  – Cell flow and mass transfer optimization
  – Assembly of single-cell membrane-electrode assemblies
- **Task 2 - Single-Cell Characterization Testing**

  25% Complete

  – Upgrade test facility (instrumentation, 80°C, 6 bar)
  – Design and assemble single-cell electrolyzers
  – Test up to three different single-cell electrolyzers
- **Task 3 - Process Modeling & System Analysis**

  30% Complete

  – Mass and energy balances to support testing
  – Flowsheet optimization and electrolyzer cost analysis

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Accomplishments

- **Process Design Updated**
  - Improved system design with higher process efficiency of >42% (LHV)
  - Three patent disclosures prepared
- **Characterization Testing of Electrolyzer Conducted**
  - Ambient pressure SO2 Electrolyzer Test Facility designed & commissioned
  - Two PEM-based SO_2-depolarized electrolyzers (SDE) tested
  - Proof-of-Concept established for use of PEM technology for SDE
- **Design and Test Plan for Pressurized Testing Completed**
  - Integrated lab-scale test plan and conceptual design completed
  - Pressurized (6 bar) electrolyzer design prepared
  - Test facility upgrade design completed

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Accomplishments (cont)

- **Characterization Apparatus Assembled**
  - Laboratory apparatus for Membrane, Catalyst and Electrochemical Properties set-up
  - Safety reviews and Job Hazard Analysis completed
  - Test samples of various components received
- **Pressurized Test Facility Under Construction**
  - Test plan completed and issued
  - Increased temperature and pressure design completed
  - Pressure Protection reviews in progress – finalization of rupture disc and pressure relief valve caused 30-day delay
- **Industrial Partners Identified for Key Issues**
  - FedBizOps completed to identify membrane developer

Milestone Status

FY05 Milestones

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

FY06 Milestones

- M3: Test Plan for Pressurized Testing – 2/15/06 (Completed)

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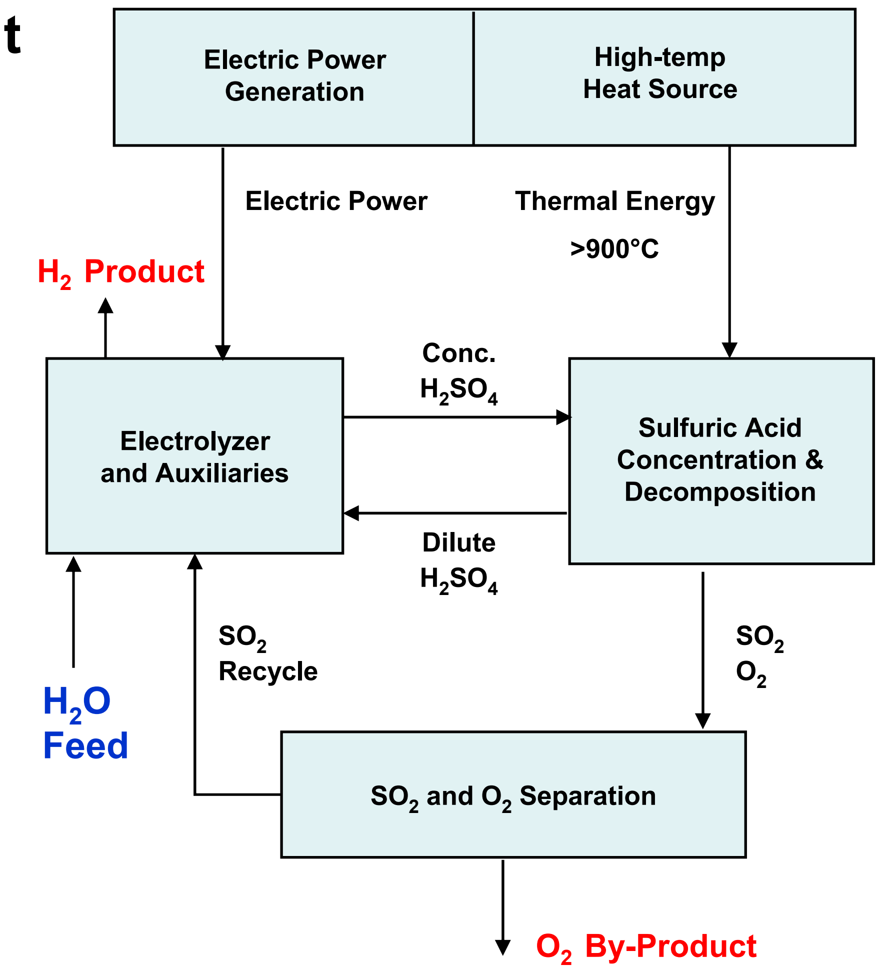
Hybrid Sulfur Thermochemical Process

- **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



HyS Reactions

$$H_2SO_4 \leftrightarrow H_2O + SO_2 + \tfrac{1}{2}O_2 \qquad (1)$$

(thermochemical; 800-900 °C)

$$SO_2 + 2\,H_2O \rightarrow H_2SO_4 + H_2 \qquad (2)$$

(electrochemical; 80-120 °C)

Net Reaction: $$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad (3)$$

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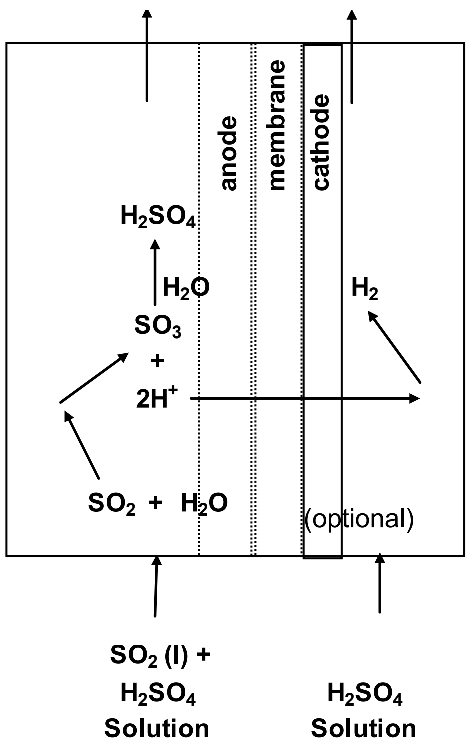
HyS Electrolyzer Concept

- Sulfur dioxide is oxidized at the anode to form sulfuric acid
- Reversible cell voltage reduced from 1.23 to 0.17 volts per cell
- Practical cell voltages 0.5 – 0.6 volts (60-75% less than direct electrolysis)
- Economic design requires high current density and low voltage
- Current process design dictates electrolyzer operation at 100-120 °C and 20 bar with 50-60 wt% sulfuric acid

SO_2 anode-depolarized electrolysis



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Electrolyzer Development Approach

- **Original Westinghouse cells**
  - Two compartment design with recirculating acid anolyte and catholyte
  - Carbon briquetted electrodes
  - Platinum electrocatalyst (17 mg Pt/cm2)
  - Microporous rubber diaphragms
  - Positive flow of acid from cathode to anode
- **Current design approach**
  - Build on development of PEM fuel cells and electrolyzers
  - Nafion or other proton-exchange-membranes
  - Gas diffusion carbon electrodes (<1 mg Pt/cm2)
  - Membrane-Electrode-Assembly (MEA) construction
  - Carbon flow fields
  - No acid catholyte required

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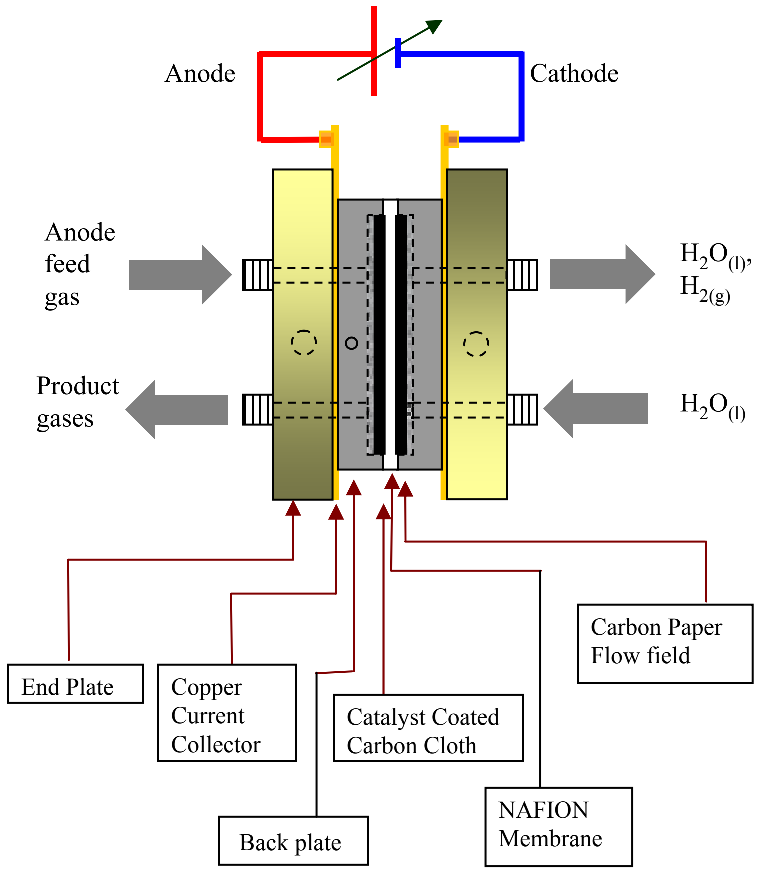
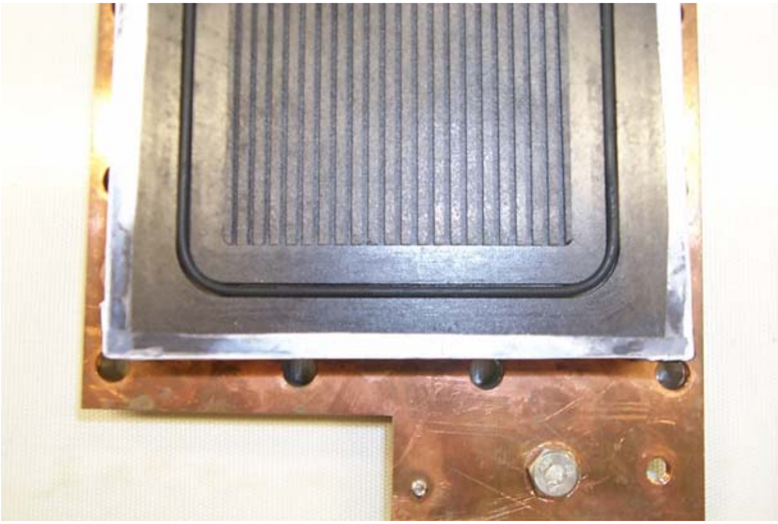
Construction of Electrolyzer





Graphite block, grooved wafer and copper connector

Ref. Weidner, *Intl. J. Hydrogen Energy*, 2005.

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Electrolyzer Development

Half-cell Reactions:

Anode: $SO_2\ (aq) + 2\ H_2O\ (aq) \longrightarrow H_2SO_4\ (aq) + 2\ H^+ + 2\ e^-$

Cathode: $2\ H^+ + 2\ e^- \longrightarrow H_2\ (g)$

Major Challenges:

- **Development of high performance membrane w/o SO2 crossover**
- **Materials and operating conditions for long-life**
- **Scale-up and potential for low-cost**

SO2-depolarized electrolyzer

SDE Test facility in FY05

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Test Electrolyzer Designs

- **Electrolyzer 1 procured from commercial PEM manufacturer**
  - Based on standard water electrolyzer
  - Wetted parts changed from 316 SS to Teflon and Hastelloy B
  - Pressure rated to 300 psig
  - Porous Titanium electrodes (could not be modified); 4 mg/cm^2 Pt loading
  - Nafion membrane
- **Electrolyzer 2 fabricated in conjunction with Univ. of SC**
  - Research type cell design
  - 50% smaller active cell area
  - Square plates; 60 psig rating
  - Carbon gas-diffusion electrodes
  - Pt electrocatalyst (0.5 mg/cm^2 Pt loading)
  - Nafion 115 membrane

Modified Commercial PEM Water Electrolyzer (84 cm2 active cell area)

Research-type Electrolyzer (40 cm2)

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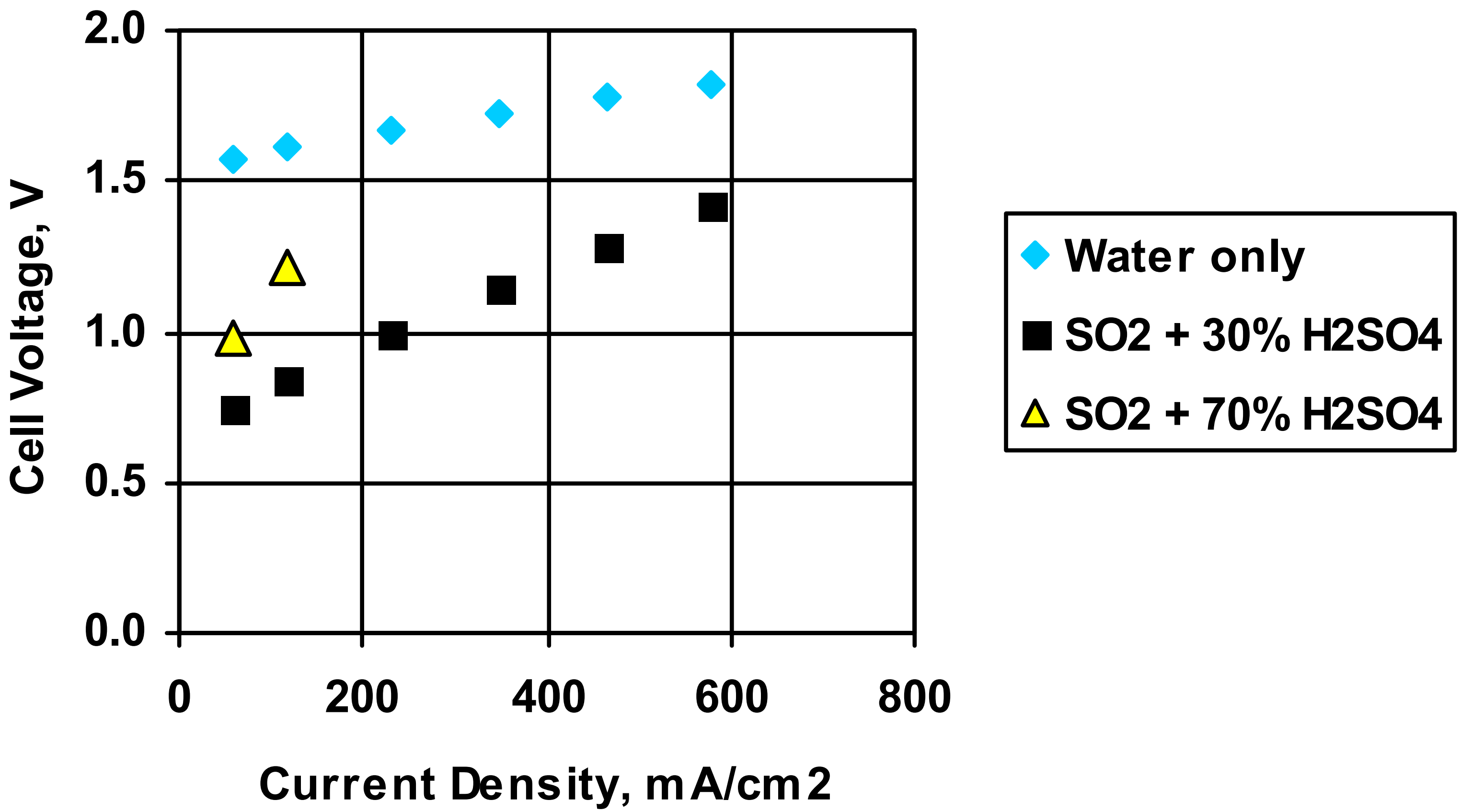
Test Results for Commercial-type Electrolyzer

Operating conditions: 25°C, atmospheric pressure



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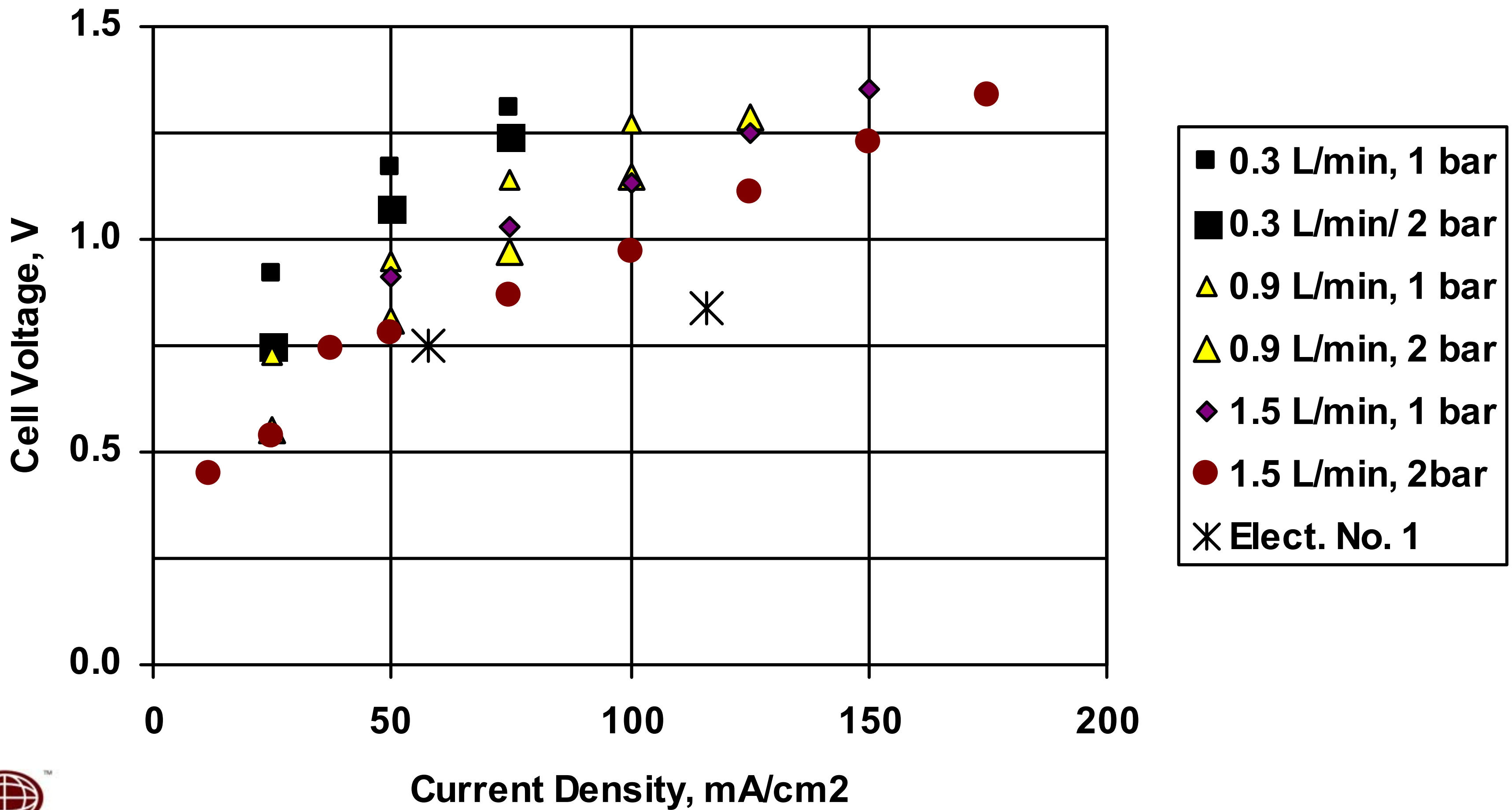
Test Results for Research Electrolyzer

Operating conditions: 25°C; 1 and 2 bar pressure



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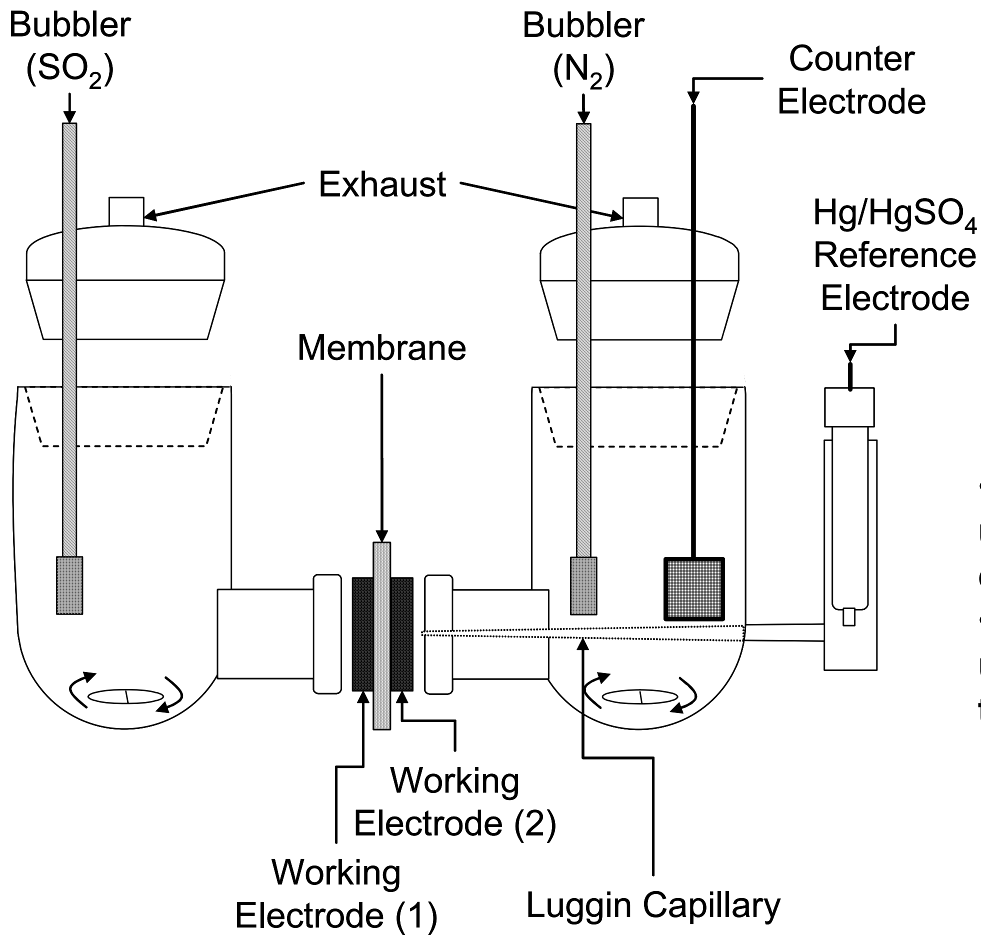
Membrane Characterization Set-up



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

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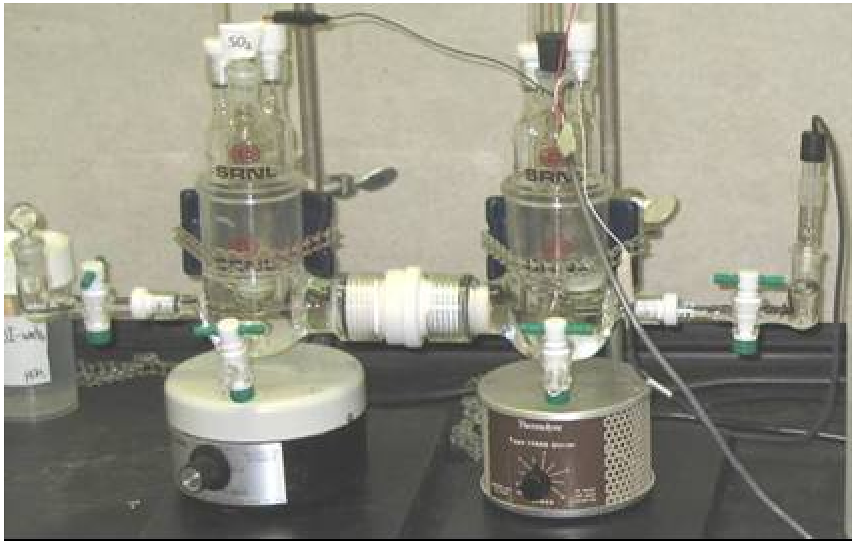
Component Characterization Test Facilities



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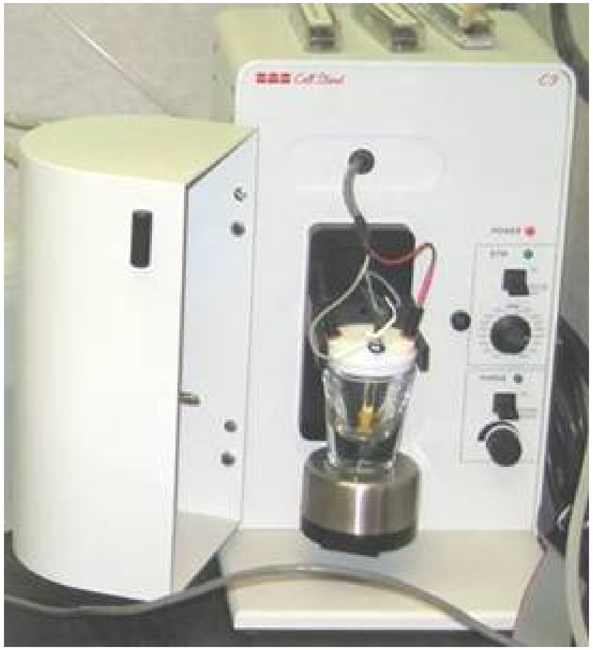

Catalyst Characterization Set-up

Electrochemical Characterization System

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Future Work

- Test and select membrane, anode/cathode and build test MEA's
- Complete SDE cell design and build test electrolyzers based on MEA's from Task 1
- Characterize performance in pressurized test facility and identify future cell development needs
- FY06 Key L2 Milestone: Complete testing and issue report by 9/15/06
- FY07 – Build SDE subsystem for integrated lab-scale demonstration of HyS thermochemical cycle
- Ongoing: Work with industry partners on improved membrane using innovative design approaches

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Summary

- **SO2 Depolarized Electrolyzer 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**
- **Successful cell development could lead to commercialization of thermochemical hydrogen production using nuclear or solar heat sources**

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Publications and Presentations

- Gorensek, M. and W. Summers, "Conceptual Design for a Hybrid Sulfur Thermochemical Process", AIChE Spring 2005 National Meeting, Atlanta, GA, April 13, 2005
- Summers, W., M. Buckner and M. Gorensek, "The Hybrid Sulfur Cycle for Nuclear Hydrogen Production", proceedings of Global 2005 International Conference on Nuclear Energy Sustainability, Paper 097, Tsukuba, Japan, October 9-13, 2005
- Summers, W. and J. Steimke, "Development of the Hybrid Sulfur Thermochemical Cycle", Proceedings of the OECD Nuclear Energy Agency Third Information Exchange Meeting on the Nuclear Production of Hydrogen, Oarai, Japan, Oct. 5-7, 2005
- Steimke, J. and T. Steeper, "Testing of an SO2 Depolarized Electrolyzer", AIChE 2005 Annual Meeting, Cincinnati, OH, November 2, 2005

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Critical Assumptions and Issues

- The SDE uses SO_2 dissolved in sulfuric acid to depolarize the anode of a water electrolyzer. Crossover of sulfur dioxide from the anode to the cathode thru the PEM membrane results in elemental sulfur formation at the cathode, reducing performance and potentially plugging the cell. Our approach to this problem includes:
  - Characterization of current Nafion membranes and other existing membranes being developed for PEM or direct methanol fuel cells
  - Cell design modifications and operating conditions changes to eliminate or minimize crossover using existing membranes
  - Development of custom-designed membranes, in conjunction with industry partners, to prevent SO_2 crossover by changing the basic polymer chemistry and cell membrane structure

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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- **Other hazards include the use of sulfuric acid under pressure**

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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Acknowledgements

- **Funding**
  - DOE-NE Nuclear Hydrogen Initiative, Project WP#SR16TC21
- **SRNL Contributors:**
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- **Westinghouse Electric Company (consultation)**
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