Electrolyzer Component Development for the HyS Thermochemical Cycle

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

Timeline
Start Date: June, 2004
End Date: October, 2013*
(work suspended 2010-2012)
50% Complete

Budget
• Total Project Funding
  • DOE Share = $5.2 M
  • Industry Cost Share = $140 K
• Funding received in FY12: $0
• Funding for FY13: $300 K (pending)

Barriers
T. Coupling Concentrated Solar Energy and Thermochemical Cycles
W. Materials and Catalyst Development
X. Chemical Reactor Development and Capital Costs

Partners
• Project Lead: SRNL
• Univ. of South Carolina and Air Products and Chemicals
• Numerous industry and university partners from previous DOE-NE work

*Project continuation and direction determined annually by DOE.
**Goal:** Process development of solar-driven high-temperature thermochemical water splitting cycle to enable integrated laboratory-scale studies followed by demonstrations utilizing solar-based heat

**Relevance:**
- Overcome barriers leading to cost-effective centralized hydrogen production from renewable sources
- Coupling of solar energy and thermochemical cycles
- Resolve major technical challenges for Hybrid Sulfur thermochemical cycle to permit reliable, cost-effective process operation at high energy efficiency
Overcoming Barriers:

- Key Step in HyS Cycle is electrochemical water-splitting based on use of an SO$_2$ depolarized electrolyzer (SDE)
- FY13 Objectives are focused on addressing major challenges of reaction kinetics, high unit output (current density), sulfur formation, and operating lifetime of PEM-type SDE
  - Demonstrate liquid-fed SDE operation at increased T&P at button-cell scale
  - Characterize various advanced PEM membranes at >120°C
  - Develop electrocatalysts that lower cell voltage and increase efficiency
- Improved SDE will result in lower capital costs, improved overall solar-hydrogen plant performance and lower hydrogen costs
HyS Process Simplified Flowsheet

- **Power Generation**
  - Electric Power: 22%
  - H₂ Product
  - H₂O, SO₂

- **Solar Receiver**
  - Thermal Energy (900°C): 78%
  - Sulfuric Acid Decomposition
  - H₂SO₄
  - H₂O, SO₂, O₂

- **Electrolyzers and Auxiliaries**
  - H₂O Feed

- **Sulfur Dioxide / Oxygen Separation**
  - O₂ By-product
  - H₂O Feed
Hybrid Sulfur Thermochemical Cycle

- Simple two-step, all-fluid cycle
- Sulfur chemistry (S-H-O species)
- Extensive development
  - R&D started in 1970’s
  - Supported by DOE Office of Nuclear Energy
- Moderate peak temperature (900°C)
- Compatible with Solar Central Receiver
- Detailed flowsheets and cost analysis completed with positive results
- Key steps demonstrated at 100 lph; need integrated lab-scale process demonstration and development of solar receiver and solar interface

Receiver/Storage Concept

HyS

SO₂ + H₂O

H₂ + H₂SO₄

SO₂ + 2H₂O

H₂SO₄

> 800°C

(> 1073K)

½O₂

H₂ + H₂SO₄

100°C

(373K)

H₂SO₄

Electric Energy

H₂

Receiver

Hot Tank

Cold Tank

Bucket Lift

SRNL
Hybrid Sulfur Process (HyS)

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

\[ \text{H}_2\text{SO}_4 \leftrightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad (1) \]

(thermochemical; 800-900°C)

\[ \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \quad (2) \]

(electrochemical; 80-120°C)

Net Reaction: \[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \quad (3) \]
**Research Status**

- **Electrolyzer based on PEM technology**
  - Focus on advanced membranes (>20 types tested)
  - Key issue is crossover of SO₂ creating sulfur
  - Goal: 600 mV at 120-140°C and 2 MPa
  - Status: 760 mV at 80°C & 700 kPa w/o S formation
  - Largest unit: 3-cell, 160-cm², 100 lph H₂

- **Acid decomposer integrated skid completed**
  - Heated section constructed of SiC with recuperation
  - Metal/SiC joints at lower temperature
  - Integrated skid with electric heating tested at 100 lph
  - Key solar feature is solid particle heating
  - Future design could use direct solar heating

- **Falling particle receiver tested at SNL**
  - Permits simple high temp heat storage
  - Operate sand/HX continuously
  - Bucket conveyor to return hot sand up tower
Step 1: SO₂-Depolarized Electrolyzer

Proton Exchange Membrane (PEM) Electrochemical Cell

SO₂ oxidized at anode to form H₂SO₄ and hydrogen ions

Reversible cell potential reduced by 87% vs water electrolysis (0.16 V vs. 1.23 V)

Practical cell voltage of 0.6 V versus 1.6-2.0 V for water electrolysis

Requires efficient thermal step to regenerate SO₂ and close the cycle

PEM cell concept permits compact design, reduced footprint, and lower cost versus earlier designs

Leverages extensive R&D and advances being done for PEM fuel cells by auto companies and others

PROGRAM GOAL: 600 mV at 500 mA/cm²
Technical Approach – SO2-Depolarized Electrolyzer

Address key challenges for efficient, long-life operation (high current density, lower voltage, no sulfur formation):

- Complete fabrication and assembly of Pressurized Button Cell Test Facility (PBCTF)
- Conduct rapid screening of membranes and electrocatalysts at elevated temperature and pressure

Prepare and characterize improved electrocatalysts

Identify advanced membrane candidates that improve performance and prevent sulfur crossover

- Work with industry and universities partners to leverage membrane developments for fuel cells and other applications

Scale-up and test in larger Single-cell Test Facility at SRNL
PEM Electrolyzer Design Concept

The PEM electrolyzer design concept involves the following components and processes:

- **End Plate**: A structural component at either end of the electrolyzer.
- **Anode**: The electrode where the oxidation reaction occurs, producing hydrogen ions (H⁺) and electrons (2e⁻).
- **Cathode**: The electrode where the reduction reaction occurs, producing hydrogen gas (H₂) and water (H₂O).
- **Diffusion Media (DM)**: A layer that facilitates the diffusion of reactants and products.
- **PEM (Proton Exchange Membrane)**: A membrane that allows protons to pass through while blocking electrons and other ions.
- **Flow Field**: Channels that guide the flow of reactants and products.
- **SO₂ + 2H₂O** enters the system, with SO₂ being converted to H₂SO₄.
- **H₂SO₄** is then converted to **H⁺ + H₂O** at the cathode.
- **H⁺** moves through the PEM to the anode.
- **H₂O** is converted to **H₂ + O₂** at the anode.
- **2H⁺** combines with electrons (2e⁻) to form **H₂**.
- **MEA Cross-section**: A microscopic view showing the thickness of the membrane, ranging from 100-150 μm.
Prior Technical Accomplishments - Electrocatalyst

- Pt/C is more stable and has greater activity than Pd/C (converse to some previous results)
- Pt-transition metal alloy catalysts (Pt/Co, Pt/Co/Ni, Pt/Co/Cr) show improvement over Pt/C
- Activation of the catalyst surface is needed for optimum oxidation kinetics
- Higher acid concentrations decrease catalyst activity
- Higher temperatures increase catalyst activity
- BASELINE DESIGN: Pt/C with higher operating temperature

Materials tested:
- Pt, Pd, Pt/transition metal alloys on carbon black
- Cyclic Voltammetry (50mV/s)
- Linear Sweep Voltammetry (5 mV/s)
Prior Technical Accomplishments - Membranes

Membrane candidates included unmodified and modified PFSA (e.g. Nafion®) and hydrocarbon and fluorocarbon base membranes

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Institution</th>
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<tbody>
<tr>
<td>Perfluorinated sulfonic acid (PFSA) – e.g. Nafion®</td>
<td>DuPont</td>
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<tr>
<td>Polybenzimidizole (PBI)</td>
<td>BASF (Germany); Univ. So. Car.</td>
</tr>
<tr>
<td>Sulfonated Diels-Alder polyphenylene (SDAPP)</td>
<td>Sandia National Laboratories</td>
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<tr>
<td>Stretched recast PFSA</td>
<td>CWRU; Vanderbilt</td>
</tr>
<tr>
<td>Nafion®/fluorinated ethylene propylene (FEP) blends</td>
<td>CWRU; Vanderbilt</td>
</tr>
<tr>
<td>Treated PFSA</td>
<td>Giner Electrochem.</td>
</tr>
<tr>
<td>Perfluorocyclobutane-biphenyl vinyl ether (BPVE)</td>
<td>Clemson University</td>
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<tr>
<td>Perfluorocyclobutane-biphenyl vinyl ether-hexafluoroisopropylidene (BPVE-6F)</td>
<td>Clemson University</td>
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SO₂ Transport Characterization Cell
Prior Technical Accomplishments - Membrane Results

- Nafion® 115 serves as baseline
- PFSA/FEP blend and the BPVE-6F membranes exhibited lower SO2 transport than Nafion®, but with somewhat lower ionic conductivity
- SDAPP had high conductivity, but also higher SO2 transport
- PBI, BPVE, SDAPP, Modified PFSA, PFSI and S-PF CB membranes exhibit reduced SO2 transport and potential for higher temperature operation (120-140°C)
Prior Accomplishments - Single Cell Electrolyzer Testing

Test Capabilities:

- Reconfigurable electrolyzer
- Nominal 60 cm² active cell area
- Pressurized test facility with liquid H₂SO₄/SO₂ feed
- Operation to 80°C and 600 kPa
- Unattended operation with remote monitoring
- Current density to 1100 mA/cm²
- Hydrogen output is 10-20 L/hr
- Over 40 MEA designs tested
Prior Accomplishments - Single Cell Electrolyzer Testing

- Tests conducted at ambient conditions and 80°C and up to 600 kPa
- 39 MEA configurations tested from 2007-2010
- Performance improved as the program progressed
- Current status is 760 mV (80°C) versus 600 mV goal
- Higher temperature and pressure operation results in lower voltages – requires new membranes
- Testing resumed in 2013 with industry support
Prior Technical Accomplishments - Major Milestones

Successfully completed Level 1 Milestones for DOE-NE three consecutive years

- M1: Demonstrate long-term operation (>100 hrs) for liquid-fed SO2 Electrolyzer (5/15/07) - Completed on Schedule
- M1: Complete multi-cell stack testing (3/31/08) - Completed on Schedule
- M1: Demonstrate SDE operation without sulfur buildup limitations (6/30/09) - Completed on Schedule
  - Completed two tests of 216 hours each; post-test examinations showed no signs of sulfur formation

DOE-NE Nuclear Hydrogen Program was discontinued in FY2010 due to redirection of high temp reactor program; work on HyS development was suspended
Technical Accomplishments – Non-DOE Funded

Ongoing collaborative research activities funded by others in FY 2013:

- Long-term single cell testing (SRNL CRADA with industry partner Air Products and Chemicals)
  - Refurbish single cell test facility and demonstrate long-term operation up to 4400 hours (six month). In progress.

- Advanced membrane testing using gas-fed SO2 electrolyzer
  - Research at University of South Carolina (Dr. John Weidner) to demonstrate use of modified PBI membranes. See results.
Technical Accomplishments – University of South Carolina

Modeling and testing with SO₂ gas-fed button-cell
Individual components of cell voltage determined by experiments and mathematical modeling
Largest losses due to kinetics at anode. Membrane resistance increases at high current due to stronger acid
Good model fit with Nafion® membranes

Cell Voltage Losses

Predicted Cell Performance

Cell Voltage Losses

Predicted Cell Performance

(80°C, 600 kPa, Nafion 212)
Technical Accomplishments – University of South Carolina

Comparison of Nafion® and PBI membranes

Water added to cathode for Nafion® and anode for sulfonated PBI (s-PBI)

Unlike Nafion®, s-PBI is not affected by high acid concentration

Increased temperature improves s-PBI performance

Product acid more dilute for s-PBI; may require alternative humidification process
# Collaborations

## Collaborations from DOE-NE work (2006-2010)

<table>
<thead>
<tr>
<th>Institution</th>
<th>Contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandia National Lab</td>
<td>Acid Decomposer – Bob Moore; Membranes – Mike Hickner</td>
</tr>
<tr>
<td>Idaho National Lab</td>
<td>Acid Decomposition Catalyst – Dan Ginosar</td>
</tr>
<tr>
<td>Univ. of South Carolina</td>
<td>Cell Design and Testing – John Weidner</td>
</tr>
<tr>
<td>Clemson, Vanderbilt, Penn State, CWRU</td>
<td>Advanced membrane electrolytes – various PIs</td>
</tr>
<tr>
<td>DuPont</td>
<td>Advanced Nafion® membranes</td>
</tr>
<tr>
<td>Giner Electrochemical</td>
<td>Electrolyzer design &amp; manufacture; Gap cell development; membranes – Simon Stone</td>
</tr>
<tr>
<td>Westinghouse, PBMR, Shaw</td>
<td>Nuclear plant interface; process design &amp; cost estimates</td>
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## Current Collaborations

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<tr>
<td>Univ. of South Carolina</td>
<td>Cell Design and Testing, Modeling, Advanced membranes – Dr. John Weidner</td>
</tr>
<tr>
<td>Air Products &amp; Chemicals</td>
<td>Single cell endurance testing – Dr. Steffen Zahn</td>
</tr>
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**NOTE:** SRNL designed/built our own electrolyzer and fabricates our own MEAs using membranes from partners.
Future Work

Proposed 2013 FCT Hydrogen Production Program

• Anticipated Funding = $300 K
• Twelve month program beginning May 1, 2013
• Conduct R&D to overcome the main obstacles for successful deployment of the Hybrid Sulfur thermochemical cycle by:
  • Identify and test improved electrocatalysts to improve efficiency
  • Identify and test high-temperature, highly selective, long-lived proton-exchange membranes
  • Demonstrate liquid-fed button-cell operation at increased temperature and pressure in order to improve reaction kinetics, utilize advanced membranes, prevent sulfur formation and improve product acid strength
Future Work – Longer Term

- **Electrolyzer Development (near term)**
  - Complete high T&P button cell test facility
  - Characterize advanced membranes
  - Develop improved electrocatalysts
  - Verify operation without sulfur build-up
  - Lifetime testing without degradation

- **HyS Process Development**
  - Integrated process demonstration
  - Scale-up to pilot plant

- **Heat Source Development**
  - On-sun demonstration with solar receiver
  - Nuclear high temperature reactor
**Project Summary**

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

**Approach** Build on previous work funded by DOE-NE. Leverage ongoing PEM fuel cell work and collaborate with membrane developers. Focus near-term efforts on SO$_2$ electrolyzer.

**Technical Accomplishments** Previous work resulted in several major milestones, including multi-cell stack demonstration; high efficiency HyS commercial flowsheet; new membranes identified; test facility modified for unattended operation; successful method developed for sulfur-free operation.

**Collaborations** Active partnership with University of South Carolina and Air Products on electrolyzer development and testing; collaborations with other industry and university partners on membranes.

**Future Work** Restart electrocatalyst development; complete and operate pressurized button-cell test facility; test new high temperature membranes, including s-PBI from USC. Continue endurance testing under industry CRADA.