Electrolyzer Component Development for the HyS Thermochemical Cycle

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2013 DOE Hydrogen and Fuel Cell Program Review

Project PD096

*University of South Carolina

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Overview

Timeline

Start Date: June, 2004

End Date: October, 2013*

(work suspended 2010-2012)

50% Complete

Barriers

T. Coupling Concentrated Solar Energy and Thermochemical Cycles

W. Materials and Catalyst Development

X. Chemical Reactor Development and Capital Costs

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)

Partners

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

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*Project continuation and direction determined annually by DOE.

Project Objectives - Relevance

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:

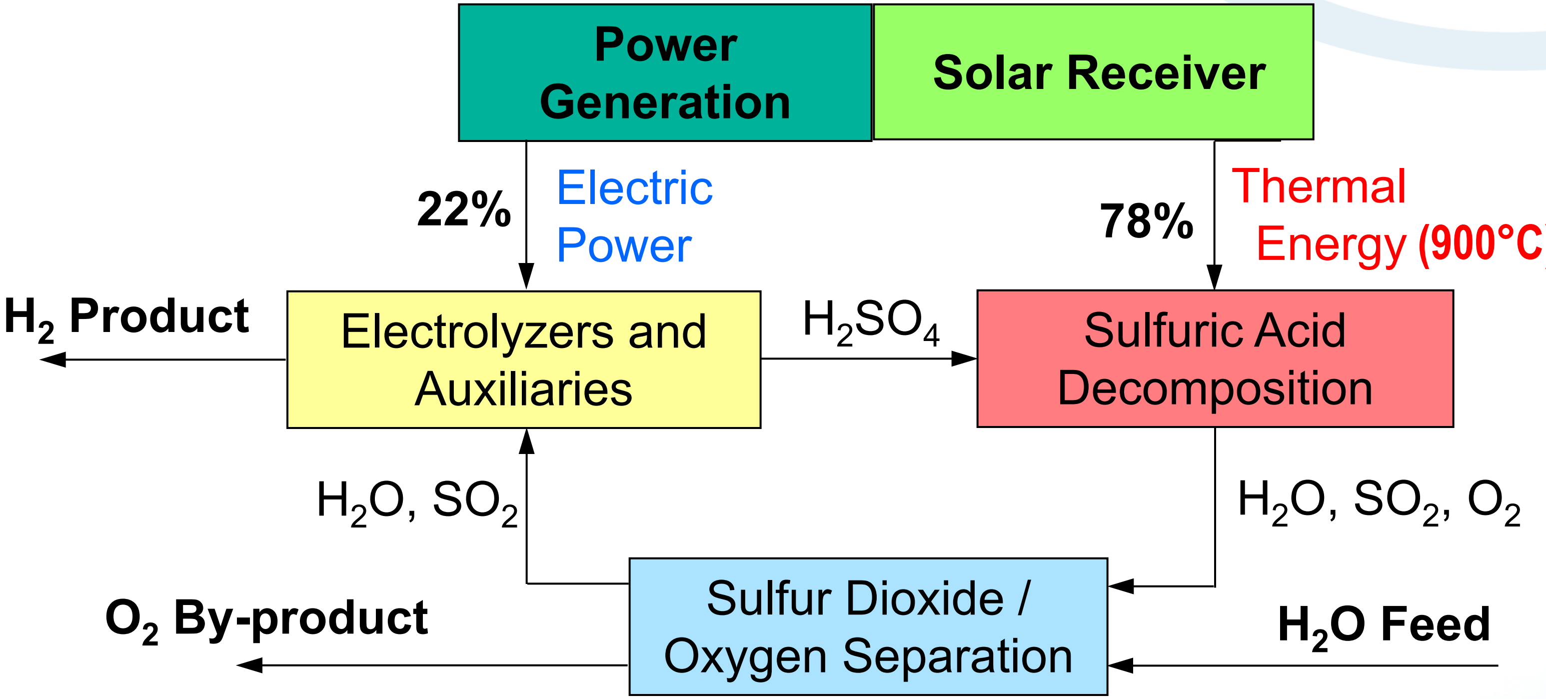
- Overcome barriers leading to cost-effective centralized hydrogen production from renewable sources
- Coupling of solar energy and thermochemical cycles
- Resolve major technical challenges for Hybrid Sulfur thermochemical cycle to permit reliable, cost-effective process operation at high energy efficiency

FY13 Objectives - Relevance

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



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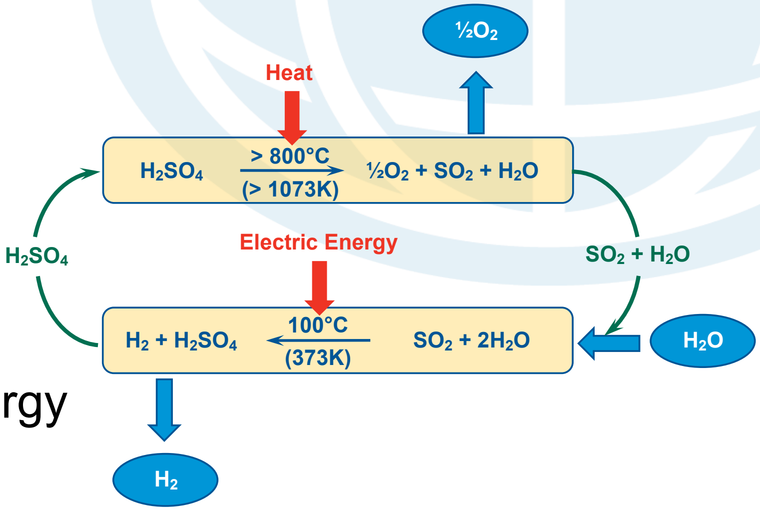
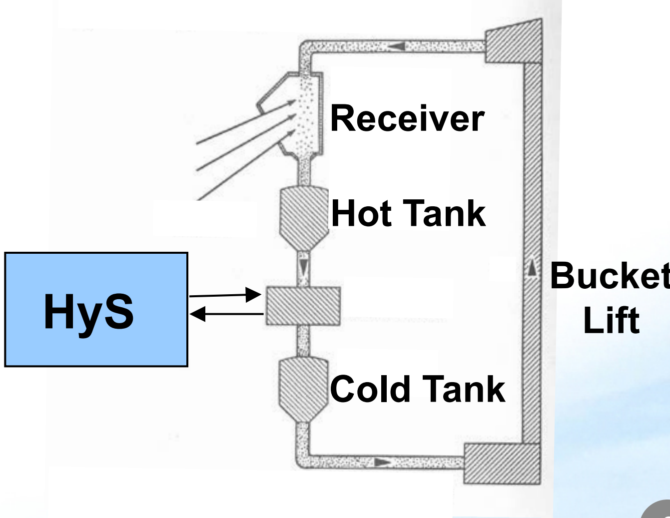
Hybrid Sulfur Thermochemical Cycle

- **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



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Hybrid Sulfur Process (HyS)

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

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

(thermochemical; 800-900ÁC)

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

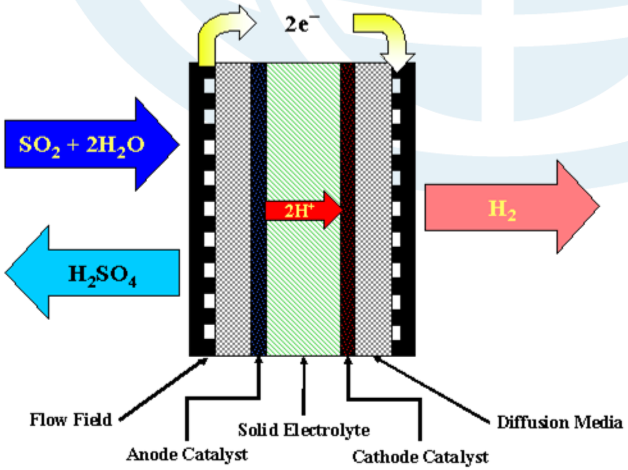
(electrochemical; 80-120ÁC)

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

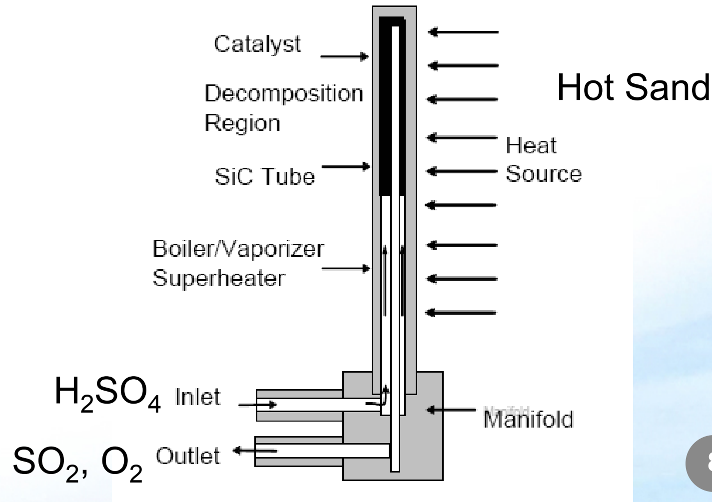
Research Status

- **Electrolyzer based on PEM technology**
  - Focus on advanced membranes (>20 types tested)
  - Key issue is crossover of SO_2 creating sulfur
  - Goal: 600 mV at 120-140ÁC and 2 MPa
  - Status: 760 mV at 80ÁC & 700 kPa w/o S formation
  - Largest unit: 3-cell, 160-cm^2, 100 lph H_2
- **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

SO_2-Depolarized Electrolyzer



Bayonet Acid Decomposer



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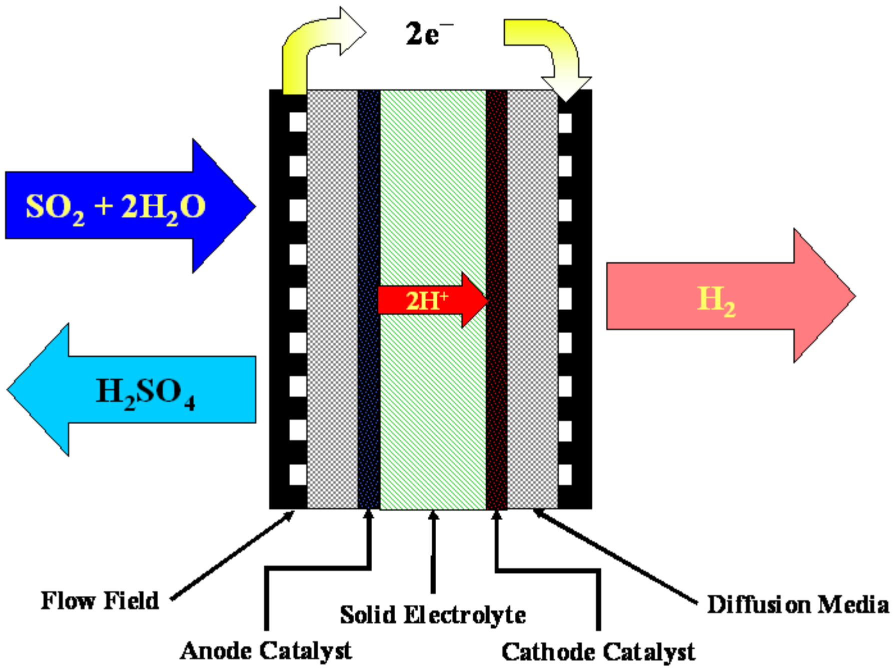
Step 1: SO_2-Depolarized Electrolyzer

Proton Exchange Membrane (PEM) Electrochemical Cell



SO_2 oxidized at anode to form H_2SO_4 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 SO_2 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/cm^2

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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

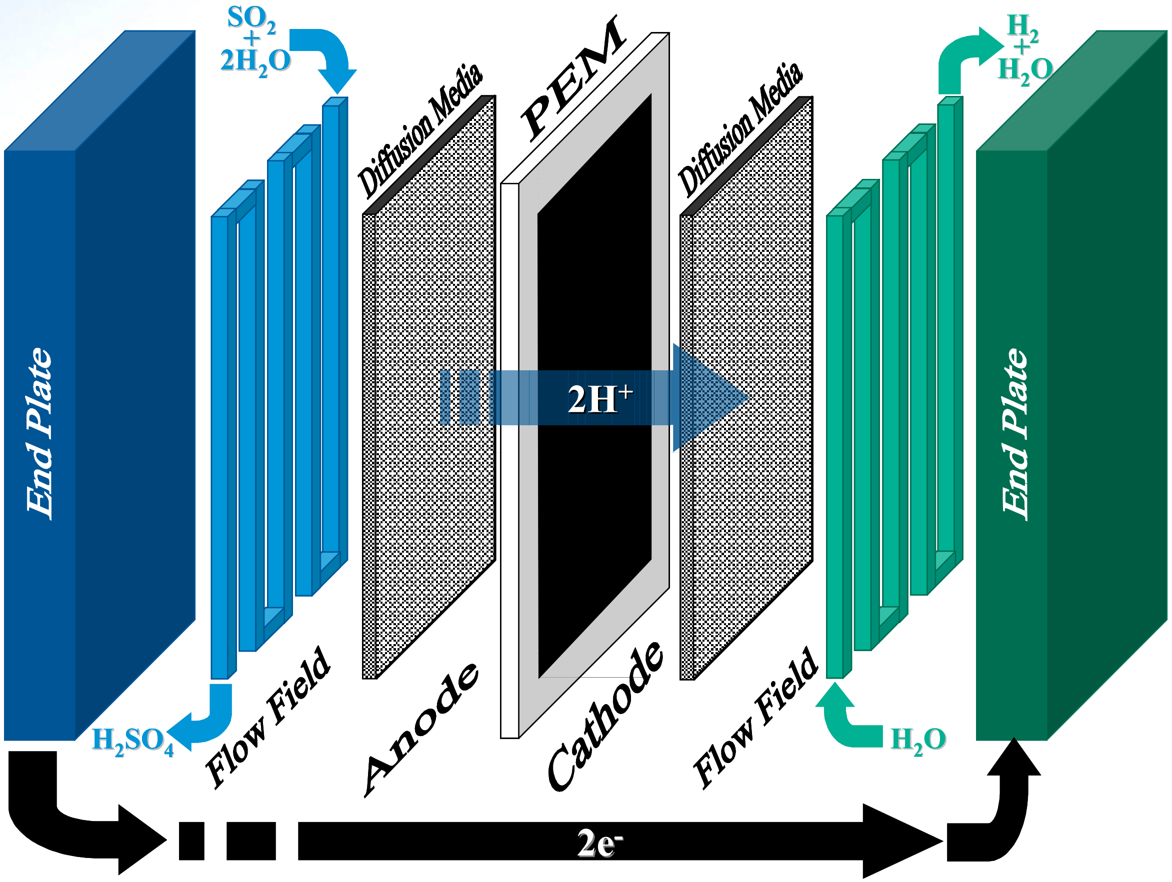
Prepare and characterize improved electrocatalysts

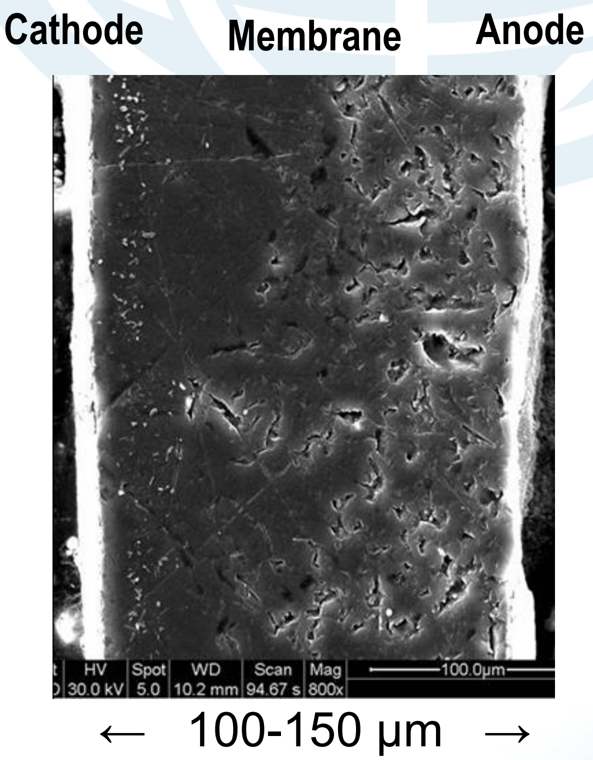
Identify advanced membrane candidates that improve performance and prevent sulfur crossover

- 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





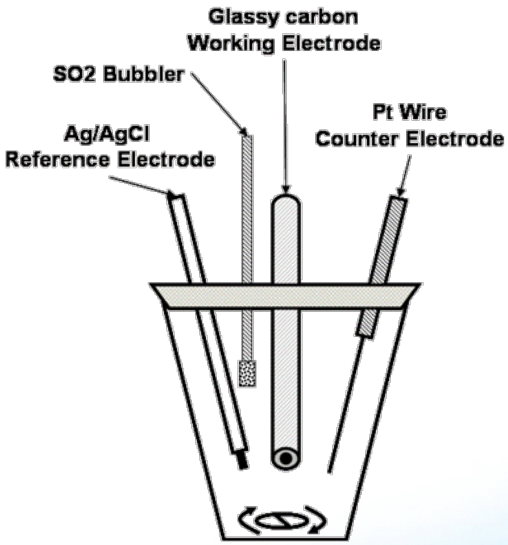
MEA Cross-section

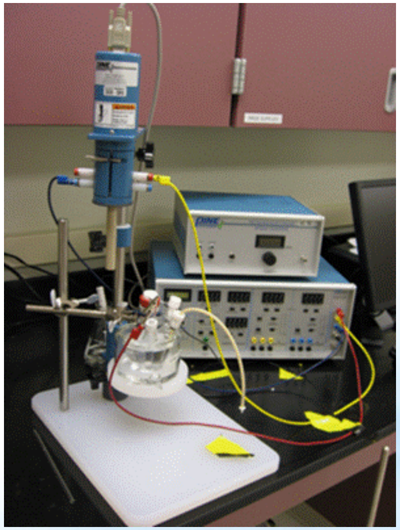
Prior Technical Accomplishments - Electrocatalyst

- 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 Voltammetery (50mV/s)
- Linear Sweep Voltammetery (5 mV/s)



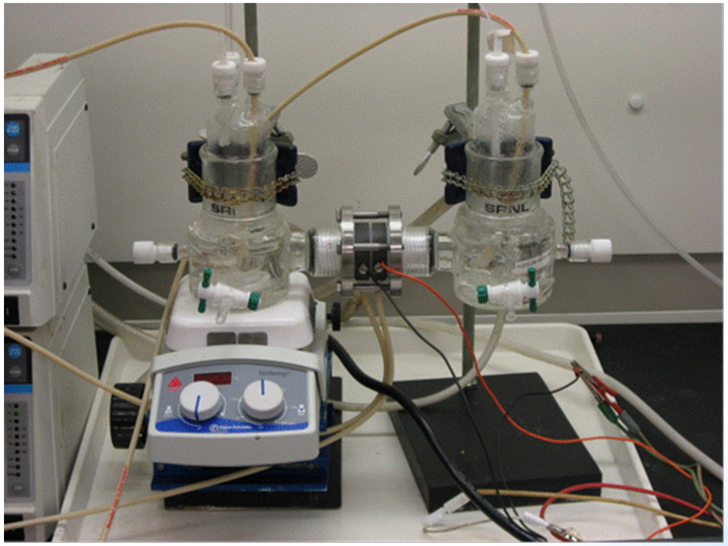


Prior Technical Accomplishments - Membranes

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

Perfluorinated sulfonic acid (PFSA) – e.g. Nafion®	DuPont
Polybenzimidizole (PBI)	BASF (Germany); Univ. So. Car.
Sulfonated Diels-Alder polyphenylene (SDAPP)	Sandia National Laboratories
Stretched recast PFSA	CWRU; Vanderbilt
Nafion®/fluorinated ethylene propylene (FEP) blends	CWRU; Vanderbilt
Treated PFSA	Giner Electrochem.
Perfluorocyclobutane-biphenyl vinyl ether (BPVE)	Clemson University
Perfluorocyclobutane-biphenyl vinyl ether-hexafluoroisopropylidene (BPVE-6F)	Clemson University

SO_2 Transport Characterization Cell



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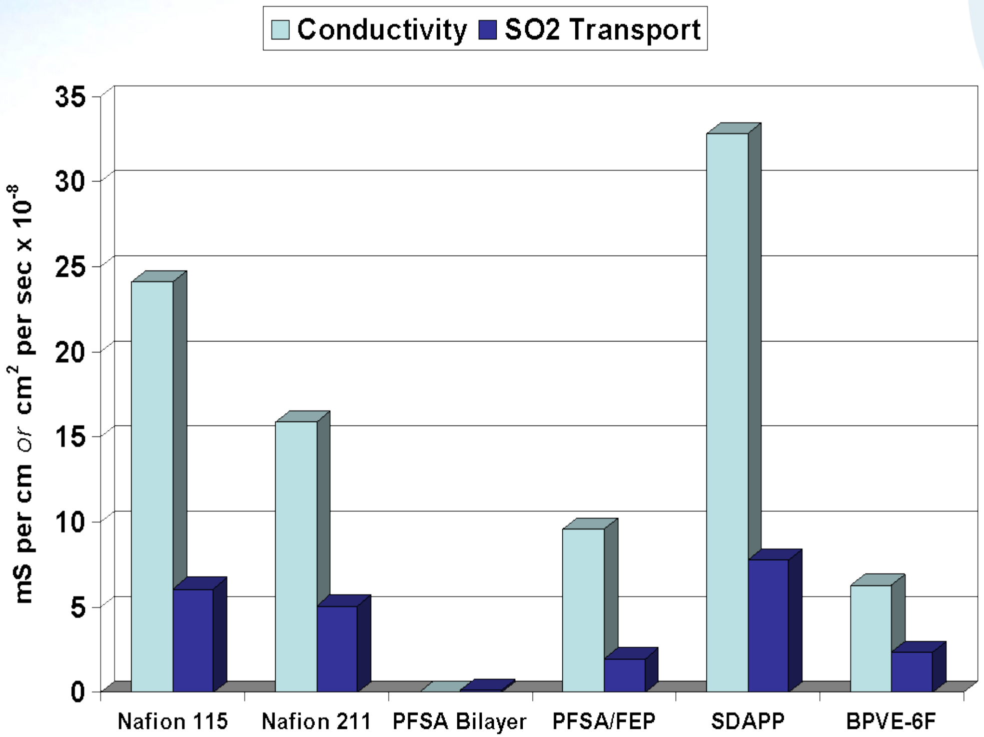
Prior Technical Accomplishments - Membrane Results



Membrane Characterization using button cells

- **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 SO_2 transport**
- **PBI, BPVE, SDAPP, Modified PFSA, PFSI and S-PFCB membranes exhibit reduced SO_2 transport and potential for higher temperature operation (120-140°C)**

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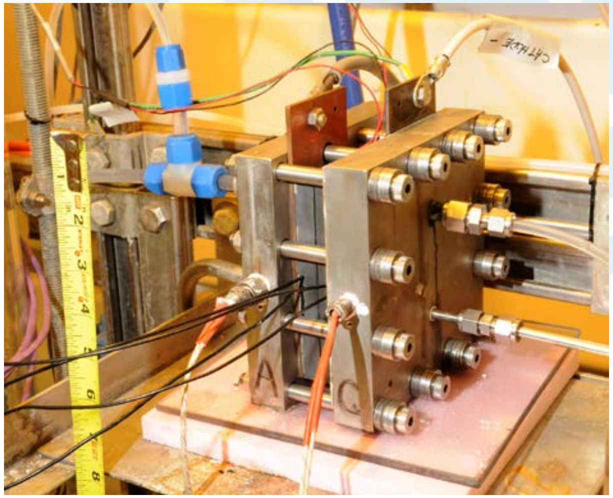
Prior Accomplishments - Single Cell Electrolyzer Testing

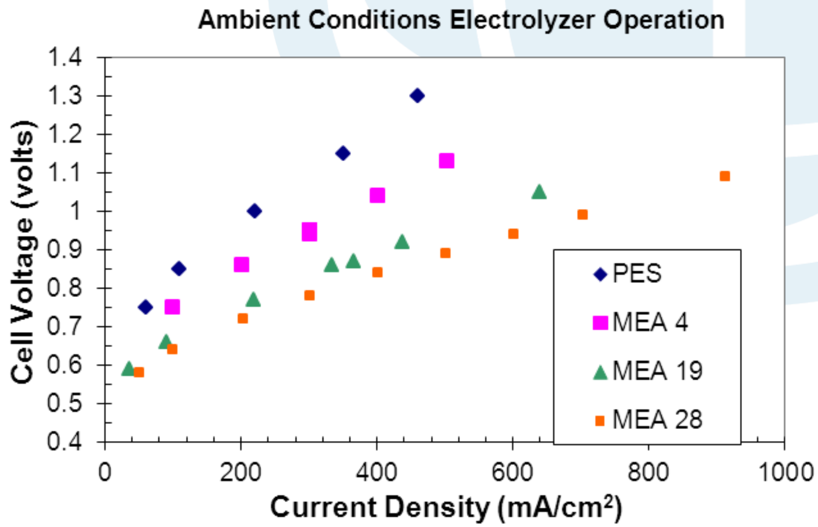
Test Capabilities:

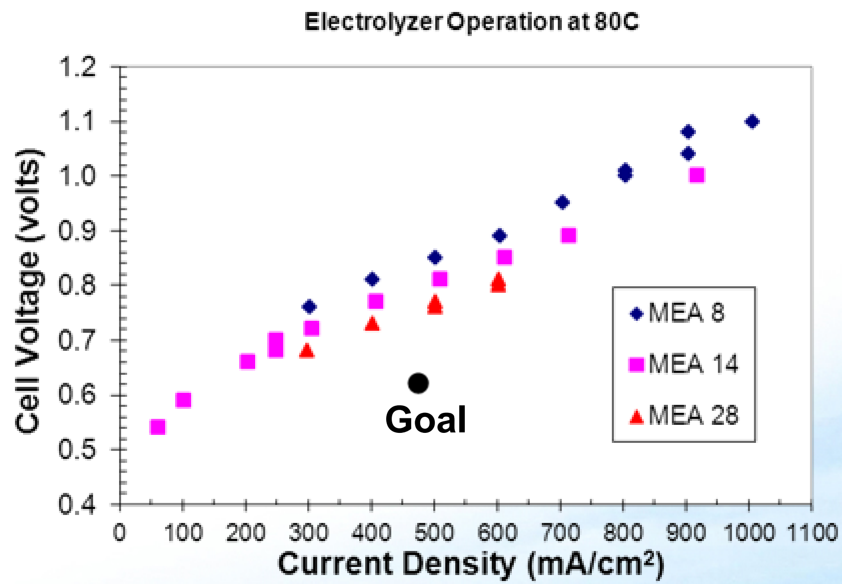
- Reconfigurable electrolyzer
- Nominal 60 cm^2 active cell area
- Pressurized test facility with liquid H_2SO_4/SO_2 feed
- Operation to 80°C and 600 kPa
- Unattended operation with remote monitoring
- Current density to 1100 mA/cm^2
- Hydrogen output is 10-20 L/hr
- Over 40 MEA designs tested



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





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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

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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.

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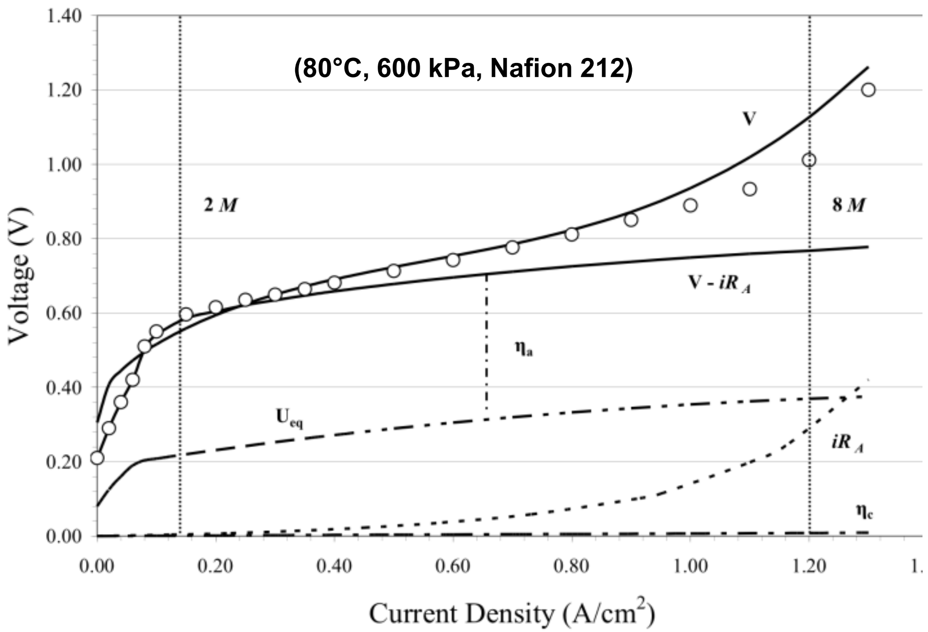
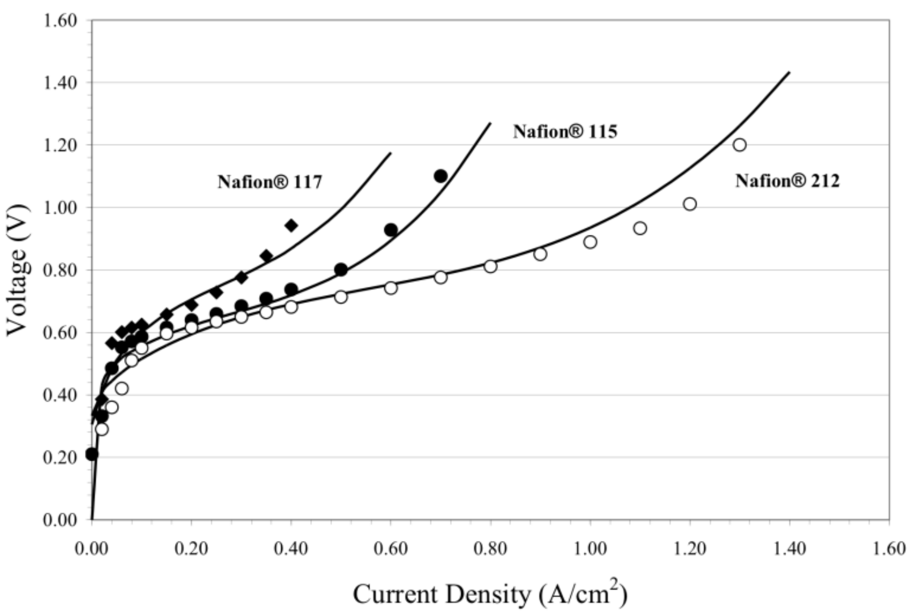
Technical Accomplishments – University of South Carolina

- Modeling and testing with SO_2 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



Technical Accomplishments – University of South Carolina

Comparison of Nafion® and PBI membranes

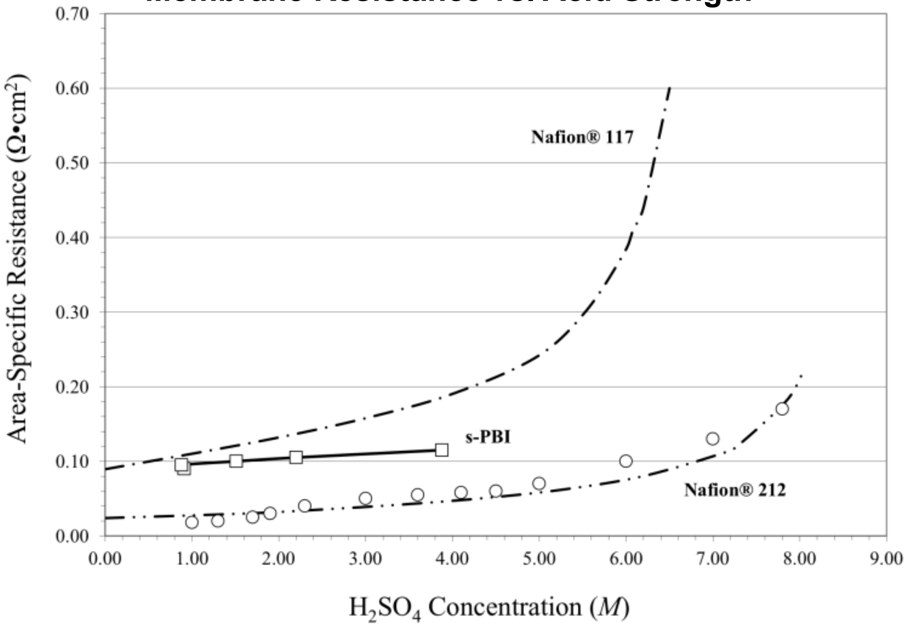
Water added to cathode for Nafion® and anode for sulfonated PBI (s-PBI)

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

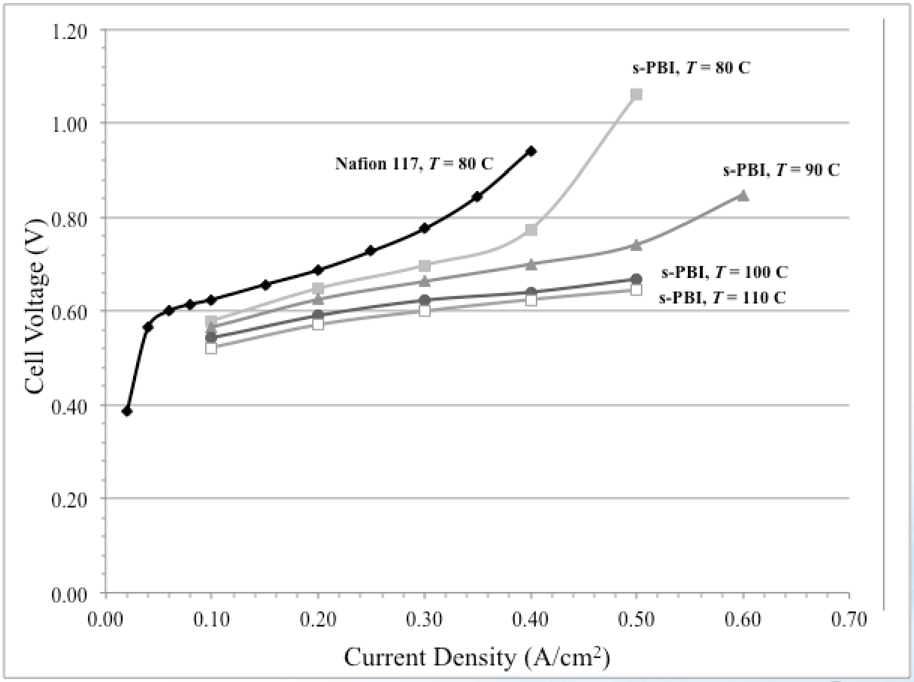
Increased temperature improves s-PBI performance

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

Membrane Resistance vs. Acid Strength



Polarization Curve Comparison



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Collaborations

Collaborations from DOE-NE work (2006-2010)

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

Current Collaborations

Univ. of South Carolina	Cell Design and Testing, Modeling, Advanced membranes – Dr. John Weidner
Air Products & Chemicals	Single cell endurance testing – Dr. Steffen Zahn

NOTE: SRNL designed/built our own electrolyzer and fabricates our own MEAs using membranes from partners.

Future Work

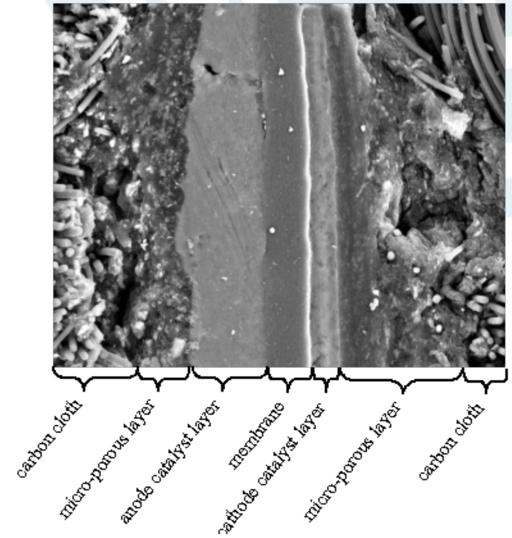
Proposed 2013 FCT Hydrogen Production Program

- 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

PEM Cell Cross-section



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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.**