Electrolyzer Component Development for the HyS Thermochemical Cycle

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Project ID PD096

Overview

Timeline

- Project Start Date: 10/01/2014
- Project End Date: 09/30/2016*

*Project continuation and direction determined annually by DOE.

Budget

FY15 DOE Funding: $500K

FY16 Planned DOE funding: $505K

Total DOE funds rec'd to date: $905K

Prior funding from DOE-NE: $5,200,000 (FY2005-FY2010)

Barriers

S. High-Temperature Robust Material

T. Coupling Concentrated Solar Energy and Thermochemical Cycles

U. Concentrated Solar Energy Capital Cost

W. Materials and Catalysts Development

AC. Solar Receiver and Reactor Interface Development

Partners

- Project Lead: SRNL
- Partners: University of South Carolina
- Collaborators: German Aerospace Center (DLR), Sandia National Laboratories, Texas Tech University

Relevance

Top-Level Objective

- Develop a low-cost, highly efficient solar thermochemical hydrogen (STCH) production process capable of achieving a hydrogen cost at the plant gate of <\$2 per kilogram of H_2

Project Objectives

- Develop highly efficient process designs for coupling the Hybrid Sulfur (HyS) thermochemical process with a concentrated solar power (CSP) system
- Demonstrate SO_2-depolarized electrolysis (SDE) using high-temperature proton-exchange membranes (PEMs) and improved electrocatalysts that permit high efficiency hydrogen production

Fiscal Year 2016 Objectives

- Analyze and select a baseline plant design that utilizes high-temperature solar heating, energy storage and permits 24-hour hydrogen production (Barriers S, T and AC)
- Develop Aspen Plus™ process flowsheet models, calculate plant performance and efficiency
- Estimate capital and O&M costs for a commercial plant and utilize the H2A analysis tool to determine projected hydrogen production costs for 2015 and 2020 design concepts (Barrier U)
- Utilize the Pressurized Button Cell Test Facility (PBCTF) to test candidate high-temperature PEMs and demonstrate SDE performance improvements of 50 mV (FY15) and 80 mV (FY16) over performance with the baseline Nafion® PEM (Barrier W)

Approach

Build on HyS Development Funded by DOE Nuclear Energy

- DOE Nuclear Energy office supported HyS development from 2005-2010 resulting in new concept for electrolyzer and significant progress on system and major equipment design
- Significant changes are necessary to accommodate diurnal solar heating and to maintain continuous hydrogen production
- Hybrid Sulfur (HyS) is a two-step thermochemical cycle based on sulfur oxidation and reduction
- Key reaction step is electrochemical water-splitting using an SO_2 depolarized electrolyzer (SDE)
- SRNL developed a PEM-based SDE using Nafion® membranes and Pt catalyst
- SDE performance improvements are needed to achieve the DOE goal of \$2/kg H_2 cost

Hybrid Sulfur Chemistry

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

(thermochemical; 800-900 °C)

$$SO_2 + 2\,H_2O \rightarrow H_2SO_4 + H_2$$

(electrochemical; 80-120 °C)

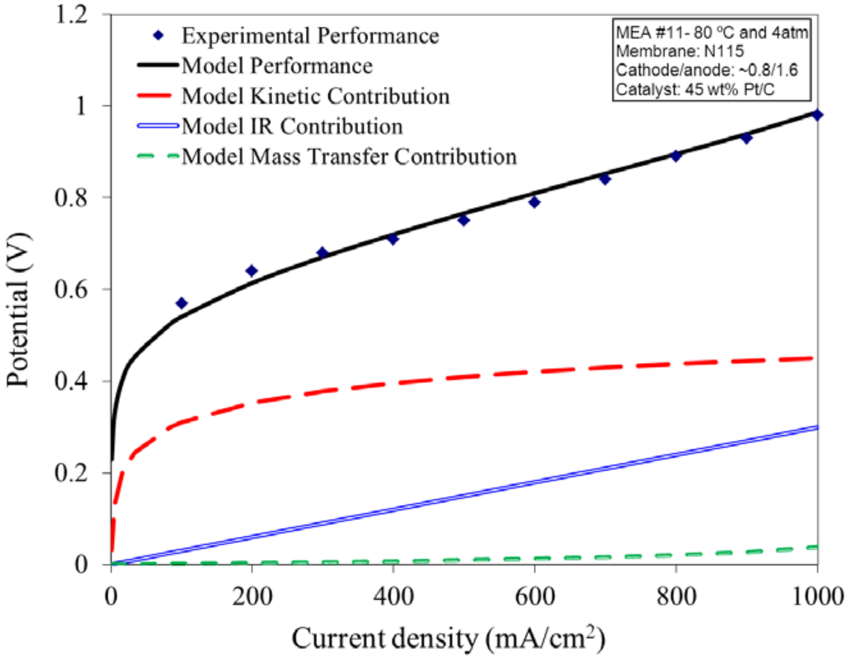
Net Reaction: $H_2O \rightarrow H_2 + \tfrac{1}{2} O_2$

All fluid process operating at <850°C

Approach

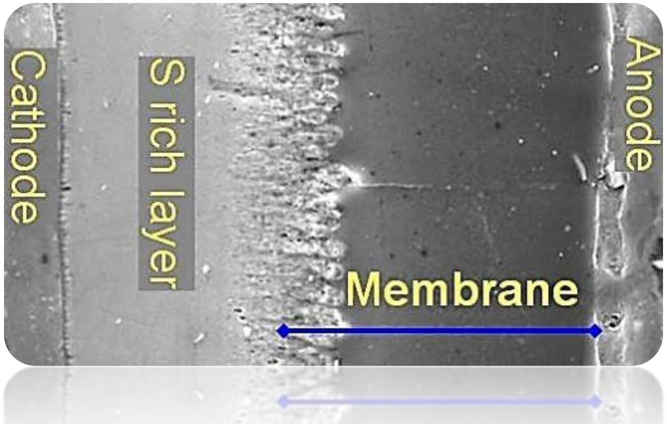
R&D to Address Electrolyzer Challenges

- Reduction of anode activation losses
- Improved membrane ionic conductivity
- Elimination of sulfur crossover

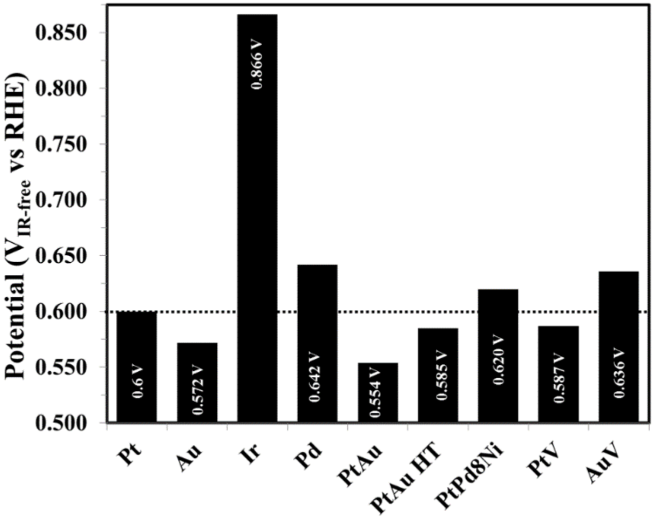


At 500 mA/cm^2

- Kinetics loss = 400 mV (54%)
- IR loss = 150 mV (20%)
- Mass transfer = 10 mV (1%)



Sulfur deposits (Steimke et al., 2015)

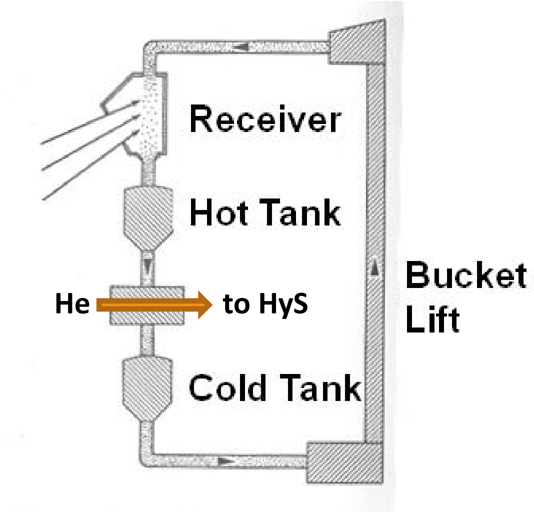


Electrocatalyst development tests

Project Integrated with Other FCTO and DOE Solar Projects

- **CSP approach shared with other STCH projects**
- **Baseline solar receiver approach leverages ongoing SunShot project by SNL**
- **Ongoing information exchange with European developers of Solar HyS**
- **Technical approach focused on two main tasks:**
  - **System Design and Analysis** – includes development of process design for solar operation; detailed flowsheets; equipment design and cost estimates; hydrogen cost estimates using H2A
  - **Electrolyzer Development and Testing** – includes operation of PBCTF, selection and testing of advanced PEMs; electrocatalyst development and testing. FY15 Go/No-Go decision achieved; further efficiency improvements targeted for FY16

SNL Falling Particle Receiver (SunShot Project)



Receiver/Storage Concept

Major Milestones and Go/No-Go Decisions

FY15 Milestone 4. Solar HyS Conceptual Design and H2A

Issue conceptual design report including optimized system design, flowsheet, performance, cost estimates and H2A analysis for 2015 Solar HyS Design. Due: 9/30/15 Status: 100%

FY15 Go/No-Go Decision

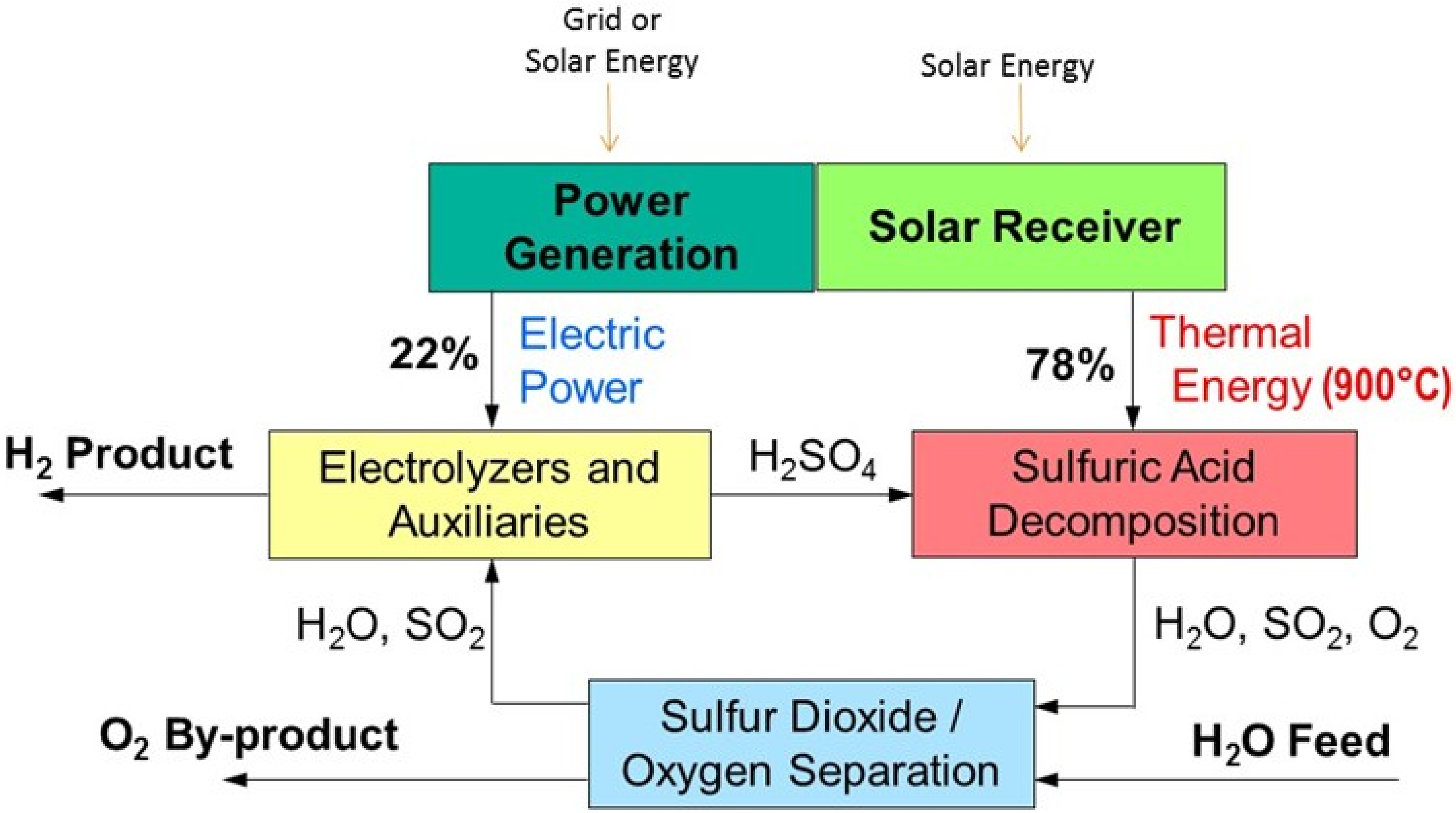
Demonstrate MEA performance for a high-temperature membrane that achieves ≥50 mV lower cell voltage than baseline Nafion® PEM. Due: 9/30/15 Status: 100% (Go/No-Go met)

Major FY16 Milestones

- Update process design for 2020 and perform techno-economic analysis demonstrating ability to meet DOE MYRDD hydrogen cost goal of <\$3.70/kg H_2. Status: 100% complete
- Perform H2A cost analysis, identify pathway and improvements needed, and perform sensitivity analyses that define the potential for Solar HyS to meet the DOE ultimate cost goal of \$2/kg H_2. Due: 6/30/2016 Status: 80% complete
- Develop a detailed design and computer model for a bayonet-type sulfuric acid decomposer and determine capability to achieve >80% thermal efficiency. Due: 9/30/2016 Status: 30%
- Upgrade PBCTF operation to permit testing at 130°C and 10 atm and demonstrate operation of an advanced MEA achieving ≥80 mV lower cell voltage than the baseline Nafion® PEM. Due: 9/30/16 Status: 40% complete

HyS Cycle Block Schematic

- HyS is a "hybrid" cycle requiring electrical and thermal energy input
- Optimization of the system requires trade-offs between the various sections



Accomplishments

System Design Trade-off Studies

- **Trade-off studies addressed key process design options**
  - Continuous vs. diurnal hydrogen production
  - Chemical (SO_2 and H_2SO_4) vs thermal energy storage
  - Direct or indirect solar heating for acid decomposition
  - Solar receiver type (e.g. Falling Particle Receiver with thermal storage)
  - Thermally-integrated or separated process reactor sections
  - Gaseous versus liquid-fed SDE operation
  - Operating conditions for SDE and acid decomposition reactors

Trade-off studies resulted in a baseline design that permits continuous H_2 production at high thermal efficiency and demonstrates potential to meet DOE hydrogen cost goals.

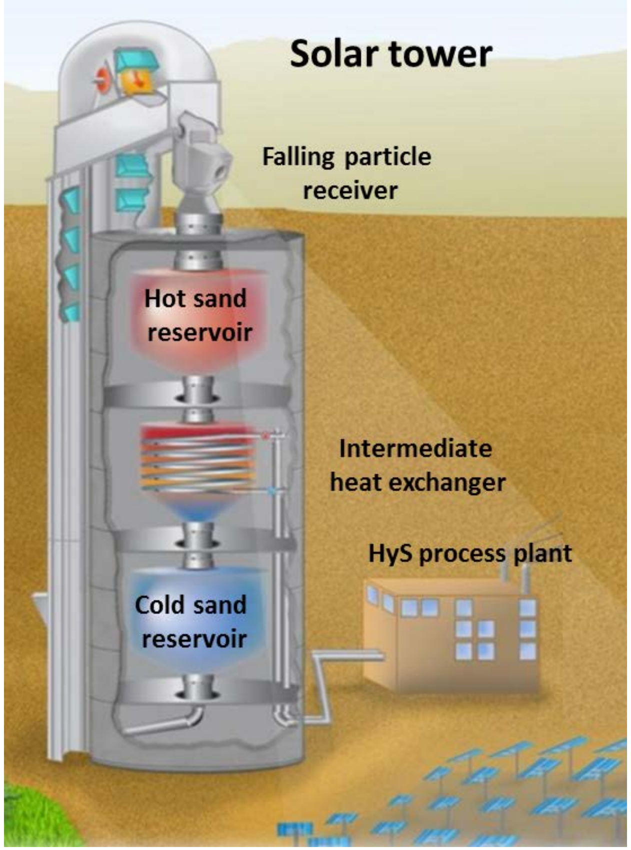
Baseline Solar Receiver Design Selected

Solar Receiver Options

- Falling Particle Receiver (Sandia National Laboratory)
  - Uses heated “sand” for thermal energy storage
- Cavity receiver with tubular heat exchanger (Brayton Energy)
  - Secondary heat transfer fluid (e.g. He) heated in receiver
- Direct solar-heated acid vaporizer and decomposer (DLR)

DLR 100 kW Solar H_2 Receiver

CSP Test Facility at Sandia



Falling Particle Receiver

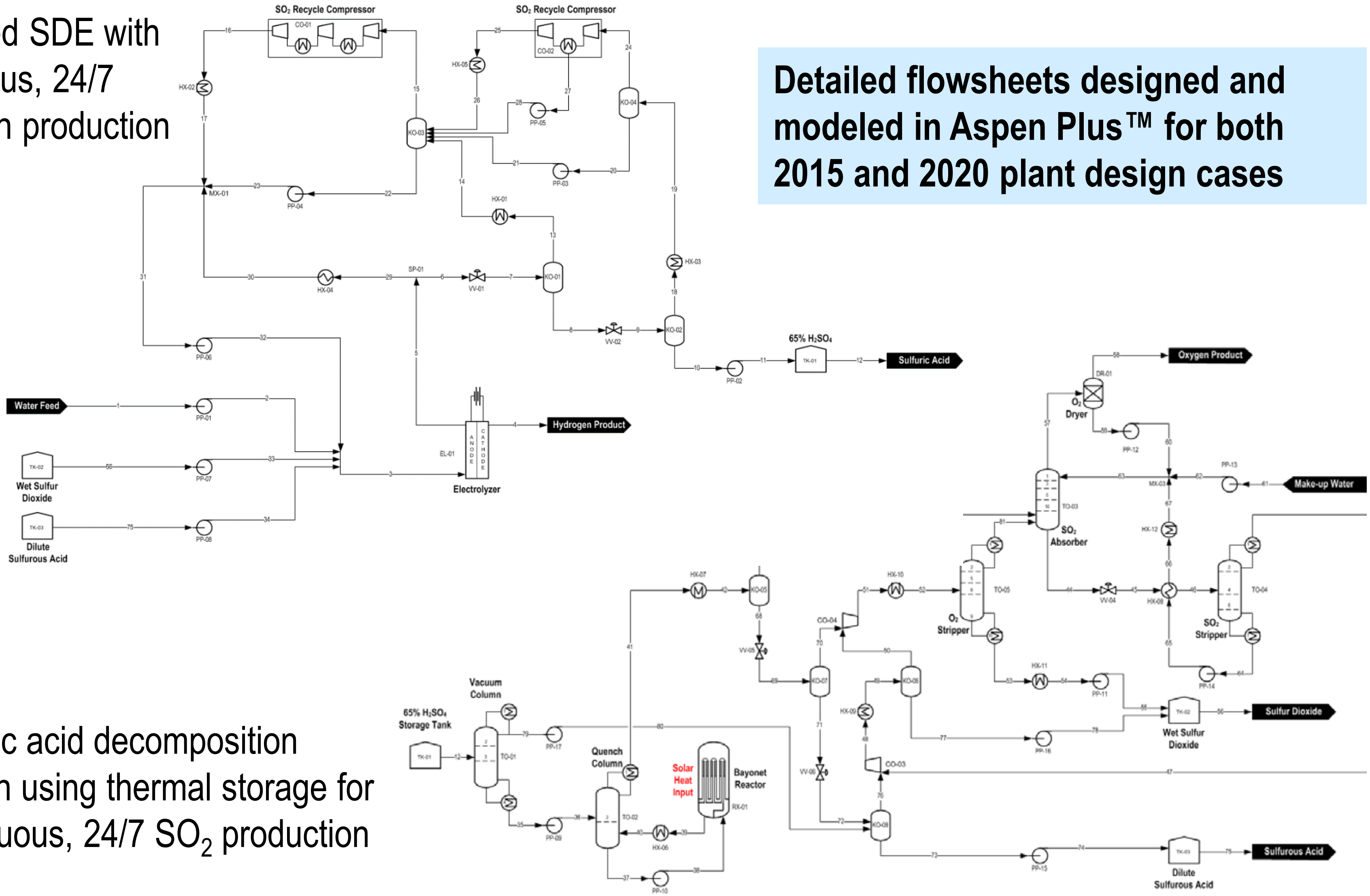
FPR leverages other DOE work and permits high-temperature heat storage for 24-hour hydrogen plant operation

Accomplishments

Solar HyS Process Design

Liquid-fed SDE with continuous, 24/7 hydrogen production

Detailed flowsheets designed and modeled in Aspen Plus™ for both 2015 and 2020 plant design cases

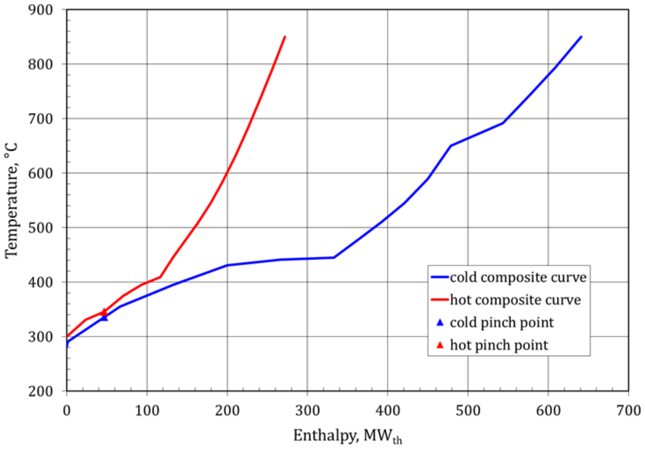


Sulfuric acid decomposition section using thermal storage for continuous, 24/7 SO_2 production

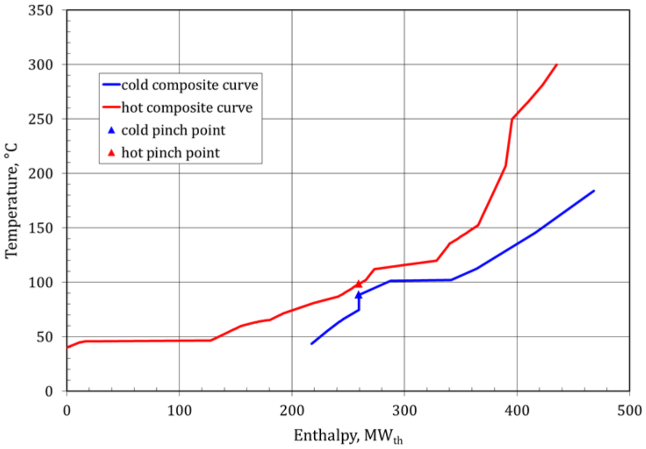
Accomplishments

Realistic Design Achieved Through Pinch Analysis

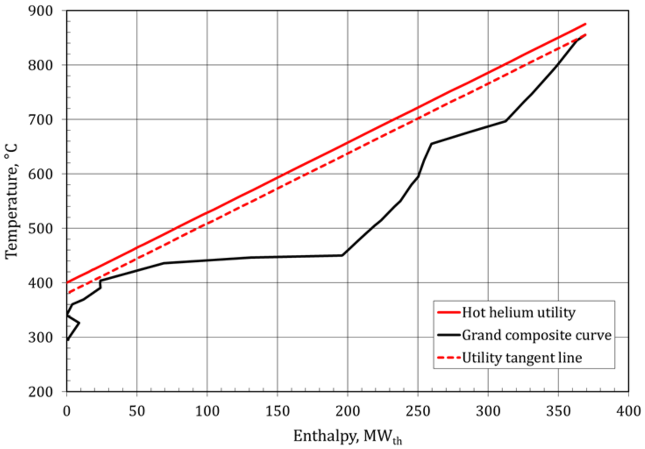
Composite heating and cooling curves, bayonet reactor, 1-kmol/s SO_2, 875°C He peak temperature, 14.1-bar feed pressure, 280.7°C feed temperature, 1-bar ΔP



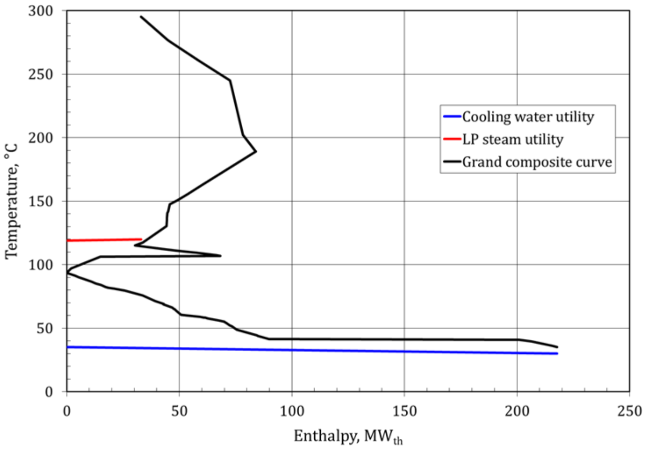
Composite heating and cooling curves for integrated flowsheet (heat exchange between sections allowed)



Utility composite curves, bayonet reactor, 1-kmol/s SO_2, 875°C He peak temperature, 14.1-bar feed pressure, 280.7°C feed temperature, 1-bar ΔP



Utility composite curves for integrated flowsheet (heat exchange between sections allowed)



2020 Solar HyS Plant Design

Plant Design Summary

- Average output = 50 MT/day H_2
- Falling Particle Receiver Operating at 925°C
- Thermal Storage = 13 hr
- Bayonet Acid Decomposer
- Integrated Flowsheet
- 24-hr/day SDE Operation
- Electricity Provided by Offsite Solar Electric Plant
- STH Conversion Ratio = 19.1%

Design Parameters

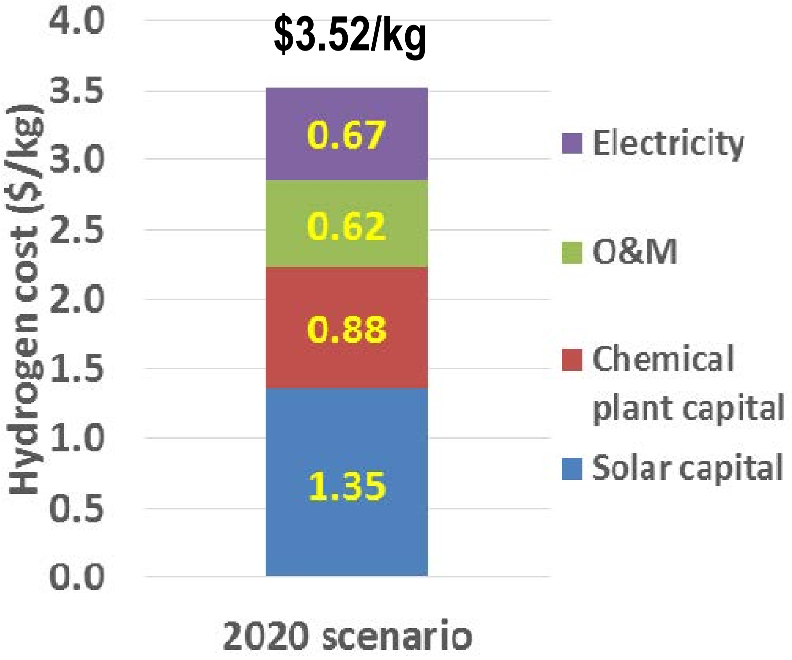
Heliostat Field Efficiency	55%
Solar Receiver Efficiency	91%
Thermal Energy Storage	99%
Acid Heat Requirement	393 kJ/mol
Solar Heat Input to Receiver	114 MW_{th}
Solar Input to Heliostats	220 MW_{th}
SDE Voltage	600 mV
Total Electric Input	36 MW_e
Solar Electric Gen Efficiency	25%
Solar Input for Electricity	146 MW_{th}
Total Solar Input	366 MW_{th}

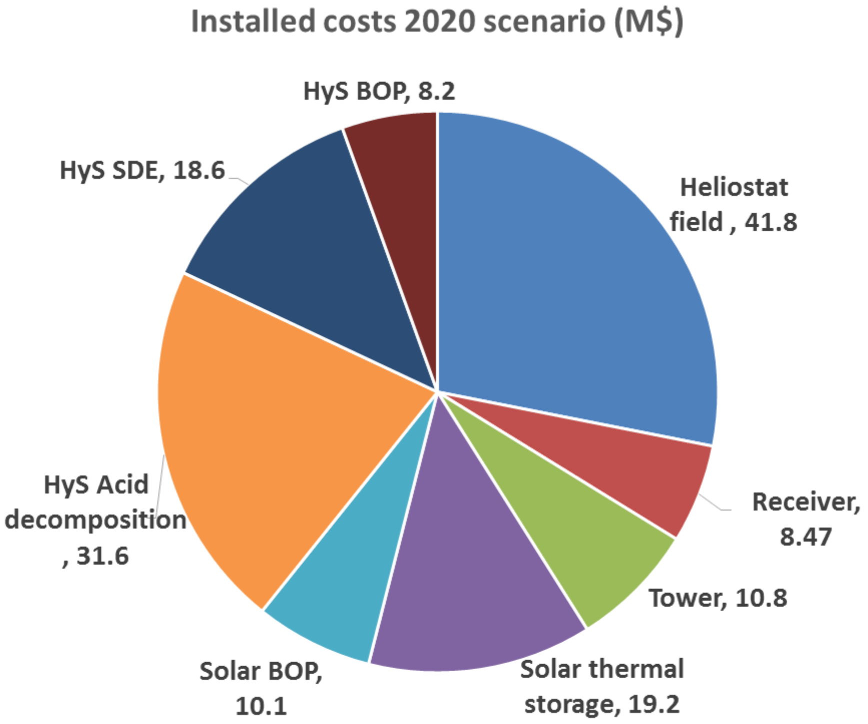
Detailed Solar HyS analysis shows promising STH conversion ratio (slightly below DOE 2020 goal of 20%, limited by solar electric generation efficiency)

Accomplishments

H2A Analysis for 2020 Design Case

- **2020 design case assumes performance and durability beyond currently demonstrated capabilities**
- **Solar plant performance and costs (heliostats, receiver, etc.) based on SunShot 2020 goals**



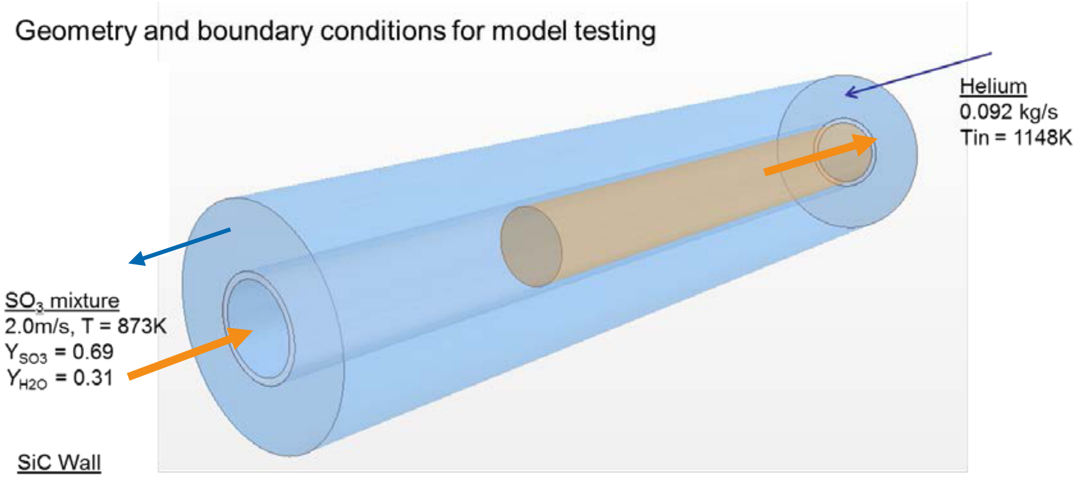


2020 boundary analysis shows potential to meet DOE intermediate goal of $3.70/kg H_2

Accomplishments

Bayonet reactor modeling initiated

Geometry and boundary conditions for model testing



SiC Wall
Density = 3050Kg/m3
Thermal conductivity = 34.8 W/m-K
Specific heat = 0.67 kJ/kg-K

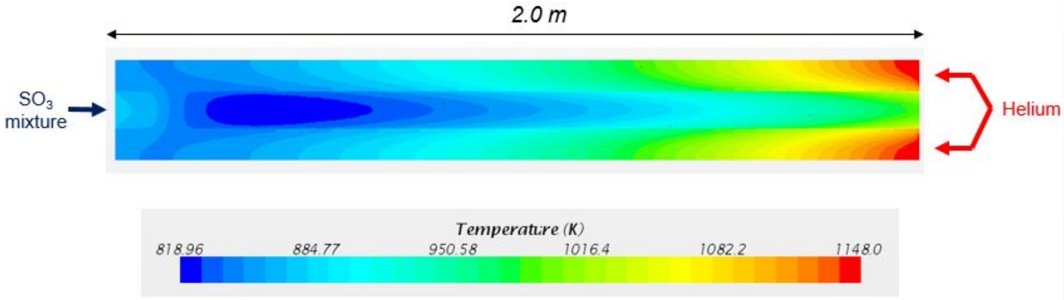
$$R_j = R_{i,kin} = -A_j T^{\beta_j} \prod_{all\ reactants} \left(\frac{\rho Y_i}{M_i}\right)^{P_{ij}} e^{-E_{aj}/R_u T} \qquad \mathrm{kmol}/\left(\mathrm{sm}^3\right)$$

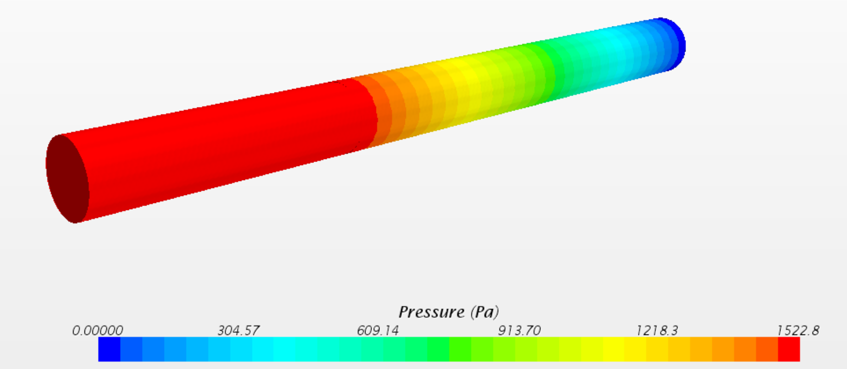
* V. Nagarajan, Intl. J. of Hydrogen Energy, 33 (2008), 6445-6455.

Reaction region

Permeability = 1E-11 m^2
Porosity = 0.5
A_j = pre-exponential factor (0.16*)
β_j = temperature exponent (0.0)
E_{aj} = activation energy (3.2E+7 J/kmol*)

- Parametric studies being carried out at University of South Carolina to validate bayonet reactor performance with helium heating
- The vaporization of H_2SO_4 and decomposition into SO_3 regions will be included in the model, with internal heat recovery
- Integrated model results due Sept 2016



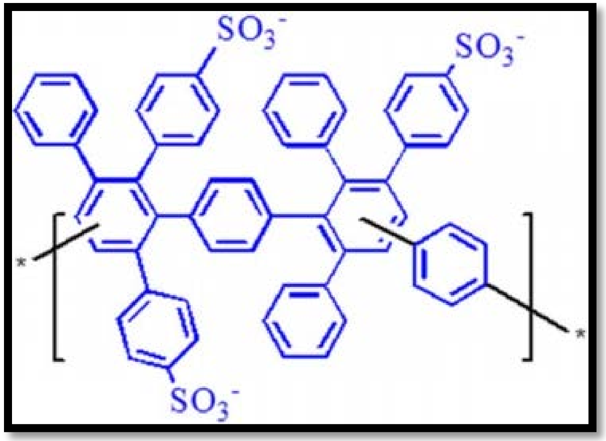


Accomplishments

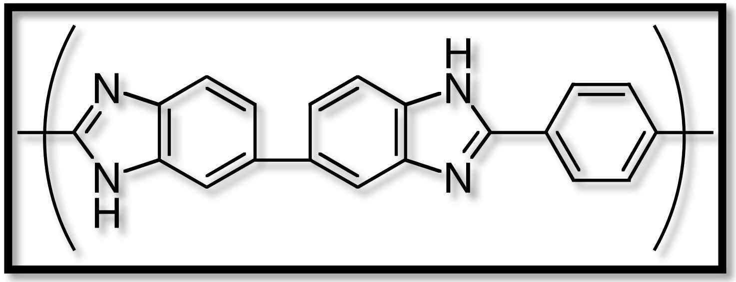
3 High-Temperature SDE Membrane Candidates Selected

High-Temperature Membrane Goals

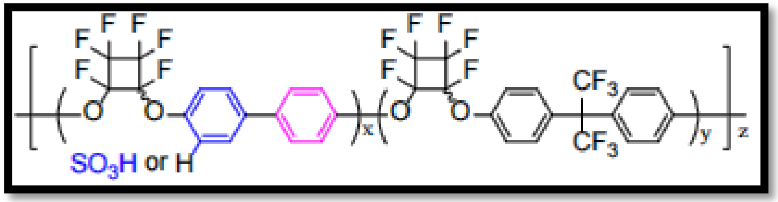
- Improve ionic conductivity
- Higher temp reduces kinetic losses
- Reduce or eliminate sulfur crossover
- Permit use of more concentrated acid
- Work with membrane developers to identify additional candidates



Sulfonated Diels-Alder polyphenylene (SDAPP)



Polybenzimidazole (PBI)

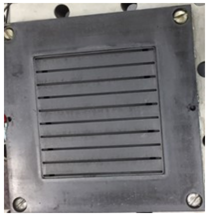


Sulfonated Perfluorocyclobutyl (S-PFCB)

High-temperature membranes increase efficiency in several ways and are key to meeting long-term electrolyzer performance goals

PBCTF Upgraded for Higher Press, Temp Operation

- Custom-designed test facility was built to test SDE components, including PEMs, catalysts, flow distributors and materials of construction
- PBCTF allows automated testing at elevated temperature and pressure (130°C and 10 atm)
- All metal parts are either polymer lined or made of tantalum or zirconium
- Many components are custom-fabricated; corrosion resistant anolyte pump in small size is particularly demanding
- Flow field was optimized using a radial design versus prior interdigitated design in larger cell



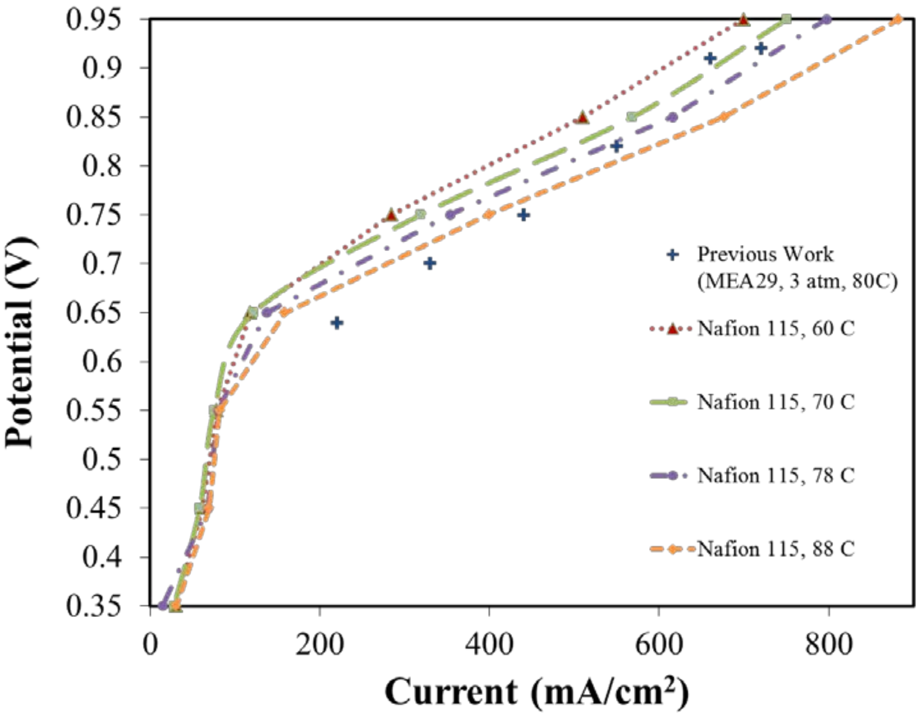
60 cm^2 cell

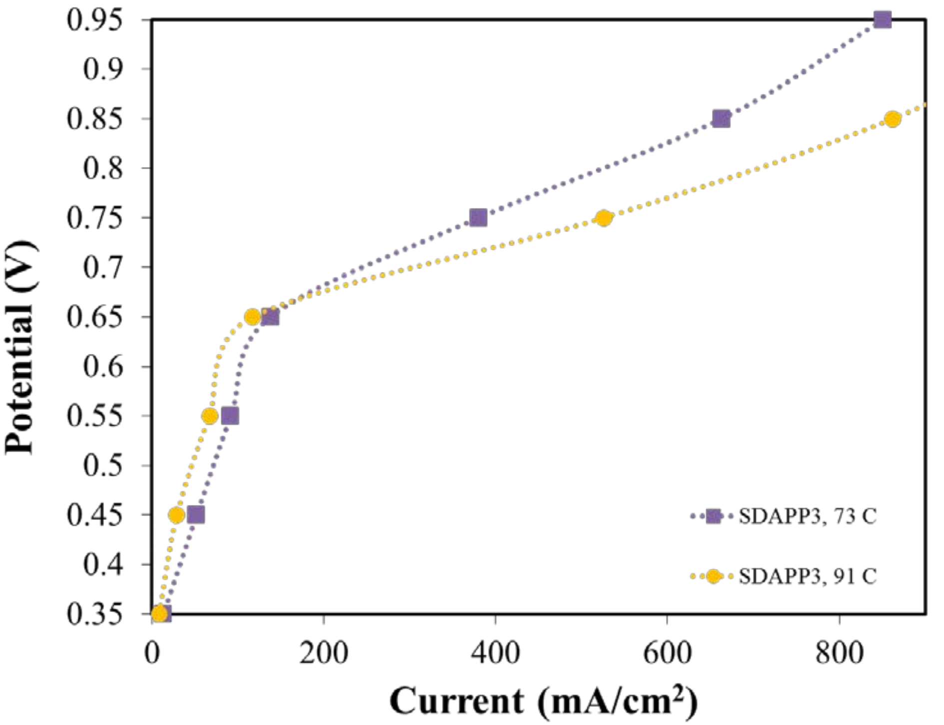
2 cm^2 cell

PBCTF is a unique and critical facility for evaluating electrolyzer components under realistic operating conditions

Accomplishments

Baseline and Advanced Membrane Test Results





- **Baseline performance in PBCTF established for Nafion® MEA at 60-88°C**
- **Results comparable with prior large cell tests**

Advanced membrane showed 50-mV performance improvement over Nafion at low temperature

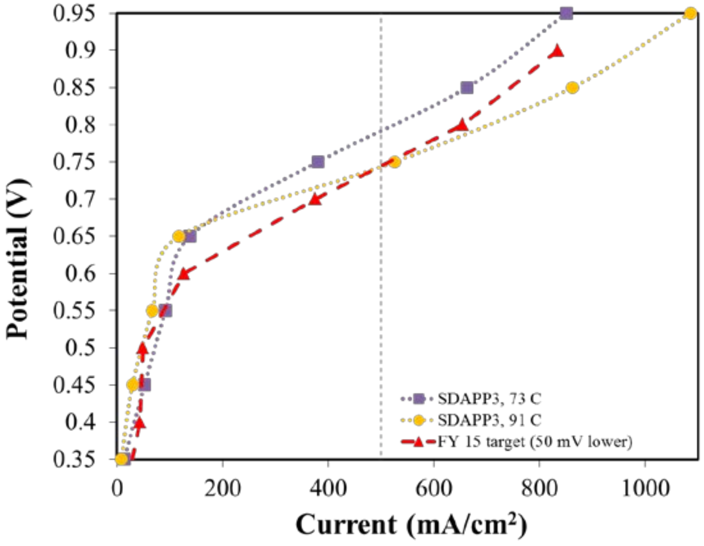
- **SDAPP MEA tested at low temp to compare with Nafion**
- **60% of losses due to kinetic overpotential – improves with T**
- **SDAPP conductance higher than Nafion at higher temperature**

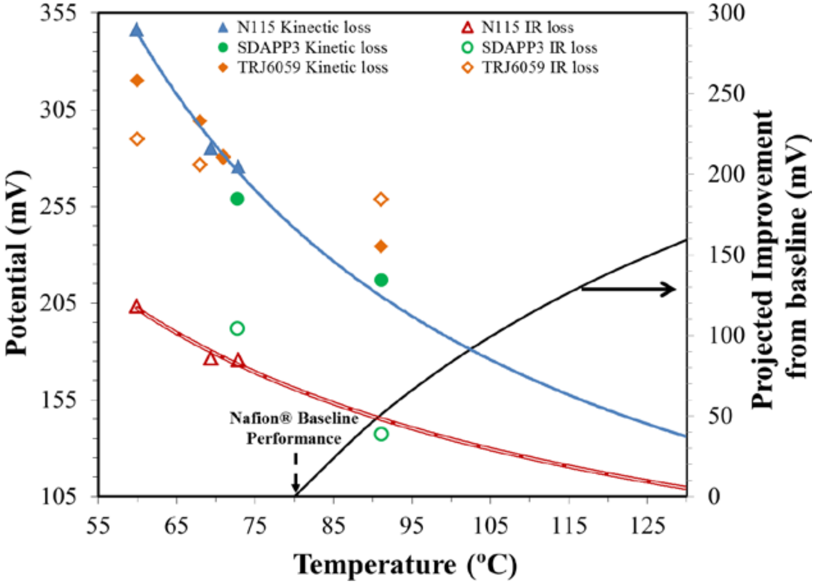
Accomplishments

GO/NO-GO Criteria Achieved

- SDAPP3 MEA meets GNG criteria of 50-mV improvement at 91°C
- Low temperature results were de-convoluted to estimate projected performance at higher temperature operation
- Potential improvement of >150 mV indicated at 130°C
- High-temperature tests planned later this year

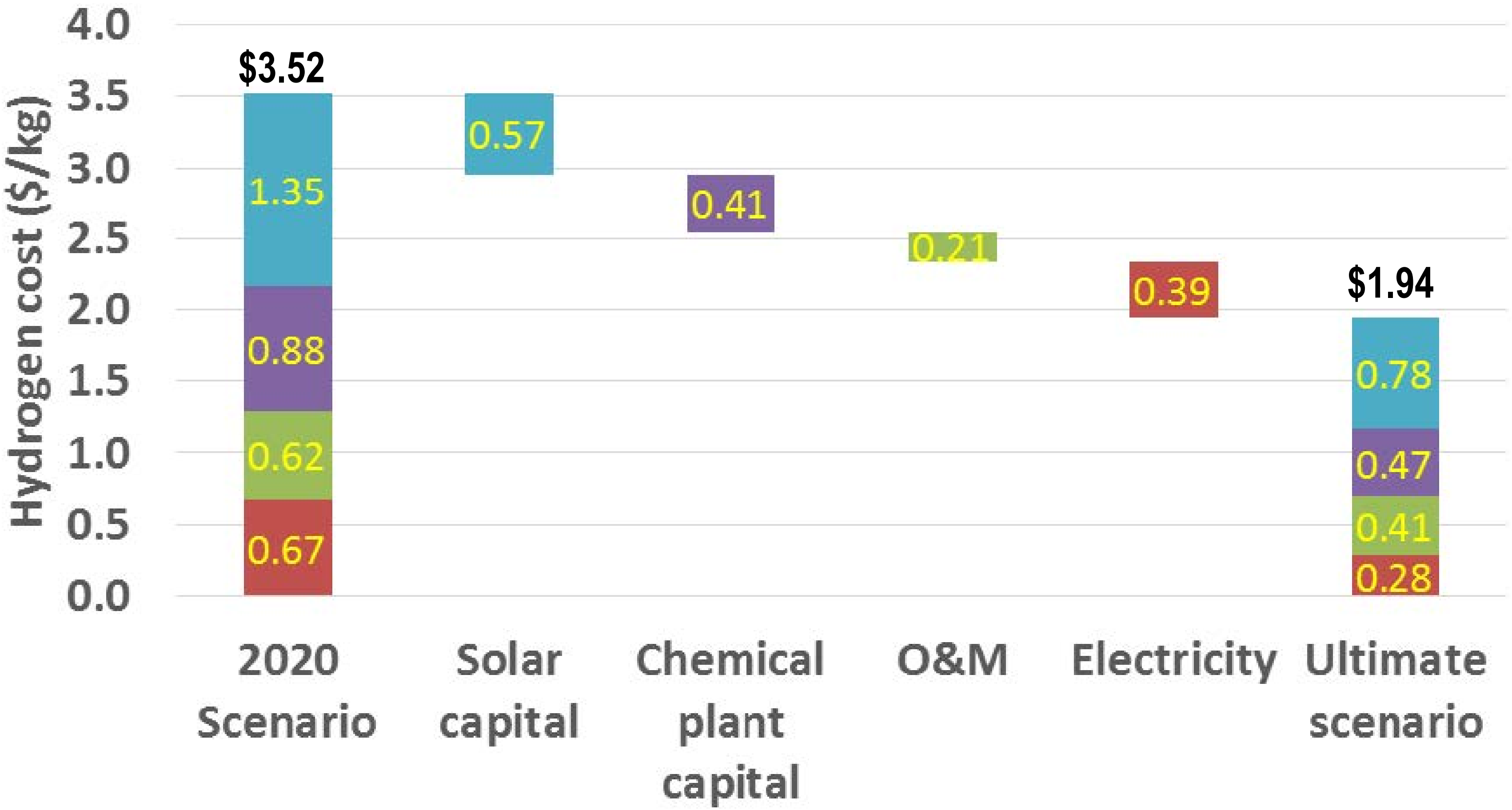
Initial PBCTF results show potential to meet SDE performance goals with advanced membranes and higher temperature operation





Accomplishments

Path to \$2/kg H_2 Production Cost



Preliminary analysis shows potential for Solar HyS to reach DOE long-term goal of \$2 per kg/H_2. More analysis is proceeding to verify this result.

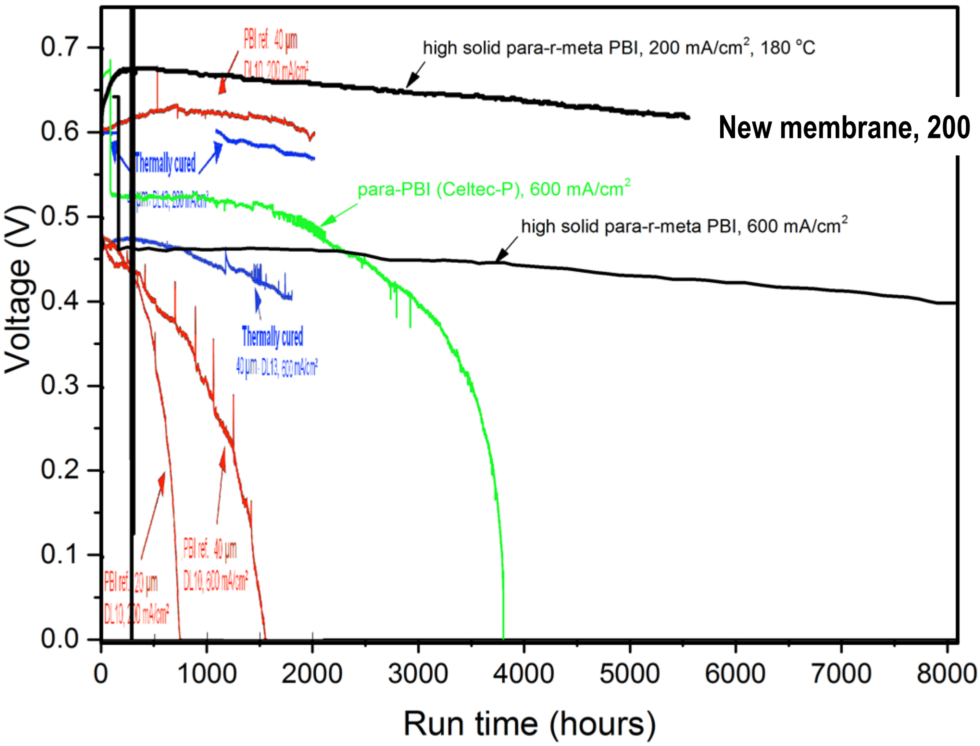
Accomplishments

Response to Reviewer's Comments

"PBI has well known stability issues and challenges in consistent manufacturing even from large well known chemical manufacturing companies."

RESPONSE: Dr. Brian Benicewicz at USC is developing new PBI membranes with support from BASF. **His work in the last few years has resulted in substantial improvements in PBI stability**. (Publication was sent to reviewers; see results on next slide). He also received a $100,000 internal grant from the university for work on the s-PBI membrane for HyS. Furthermore, the SDE membrane is always fully hydrated, unlike fuel cell operation. Long-term durability testing will be part of next year's program. In addition to PBI, SRNL is testing SDAPP and other high-temperature membranes.

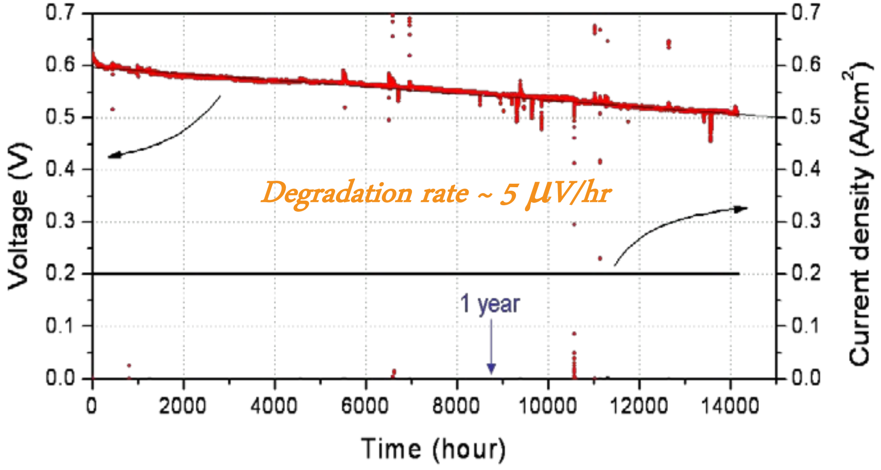
Response to Reviewer's Comments



New membrane, 200 mA/cm², 180°C

New membrane, 600 mA/cm², 160°C

120°C Endurance Test



Accomplishments

Response to Reviewer's Comments

"Future plans are poor since the vast majority of work is directed to the electrolysis process and no specific work is directed to resolve the acid decomposition process testing, evaluation and selection."

RESPONSE: Direction and funding from DOE required us to focus on the electrolyzer. However, we have added acid decomposer modeling to this year's program. We will evaluate the bayonet reactor design and determine sizing and performance for a commercial-scale reactor. Testing will be proposed for next year's program. We also continue to exchange information with DLR concerning their direct solar-heated acid decomposer being developed for the EU HyS program.

"They need to complete their H2A analysis and provide details to the DOE and reviewers"

RESPONSE: A detailed design report was completed this year and submitted to DOE. It contains extensive details on the process design, cost estimates, and H2A analysis. The AMR format does not permit enough time to cover this information in detail. We would be happy to provide copies of the report to the reviewers. See: *Corgnale, C., M. B. Gorensek, W. A. Summers, "Solar Hybrid Sulfur Water-Splitting Process," SRNL-STI-2015-00546, Revision 0, October 2015*

Collaborations

- **Advanced High-Temperature Membranes**
  - University of South Carolina (s-PBI membrane – Dr. Brian Benicewicz; MEA testing in gaseous-fed SDE – Dr. John Weidner)
  - Sandia National Laboratory (SDAPP – Dr. Fujimoto)
  - Clemson University and Tetramer Technologies (sulfonated PFCB – Dr. Wagener)
- **Solar System Design and Performance**
  - Sandia National Laboratory (Falling Particle Receiver – Dr. Cliff Ho)
  - High Temperature Solar Receiver (Brayton Energy – Jim Kesseli)
- **Acid Decomposition Reactor**
  - University of South Carolina (Bayonet reactor modeling – Dr. Shimpalee)
  - German Aerospace Center (DLR) – Dr. Martin Roeb - Information exchange regarding direct solar decomposer for EU project
- **Properties Modeling**
  - Texas Tech University (Thermodynamic Property Modelling – Dr. C.-C. Chen)

Remaining Challenges and Barriers

- Operation of the PBCTF at 130°C and 10 atm
- Testing of advanced membrane/electrocatalyst MEAs that meet performance and operating goals, including prevention of sulfur crossover
- Lifetime testing of MEAs for >1,000 hr
- Design of commercial-scale acid decomposition system meeting performance and cost goals, including the path to \$2/kg H_2
- Design and testing of the falling particle receiver (in partnership with SNL) that demonstrates capability of 900-950°C particle operating temperature
- Closed-loop operation of an integrated lab-scale HyS system

(NOTE: No thermochemical cycle has ever been tested under fully closed-loop realistic operating conditions)

Proposed Future Work

Remainder of FY 2016

- Complete H2A analysis that defines a pathway to meet the \$2/kg H_2 DOE cost goal. Identify key improvements needed and conduct a sensitivity analysis.
- Complete detailed design and computer model (including CFD and heat transfer characteristics) for a sulfuric acid decomposer based on the bayonet design.
- Using the PBCTF, demonstrate SDE performance using a high-temperature MEA that achieves an improvement of >80 mV at 500 mA/cm^2 compared to the Nafion baseline

Vision for Future HyS Work

- Demonstrate long-term durability of PBI or other selected SDE membrane
- Evaluate capability of Falling Particle Receiver to operate at 900-950°C
- Build and test a bayonet acid decomposer
- Design, construct and test an integrated HyS system

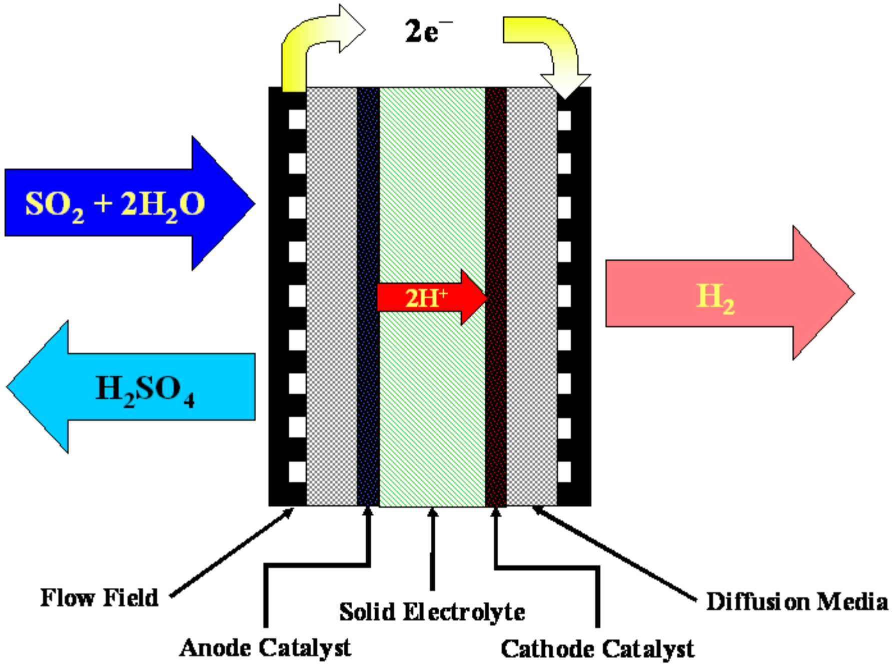
Summary

- Hybrid Sulfur is a well-known two-step thermochemical cycle that operates with all-fluid reactants and relatively low temperature (850°C) compared to other STCH cycles
- Use of the Falling Particle Receiver permits thermal energy storage and 24-hour process operation and hydrogen production
- Extensive process design and modeling resulted in detailed plant performance and equipment specifications for input into the H2A cost model
- A clear path to $2/kg hydrogen production cost was defined
- Experimental work focused on the SO_2-depolarized electrolyzer
- The Pressurized Button Cell Test Facility was used to establish baseline performance with Nafion membranes and improved performance meeting DOE GO/NO-GO goal with an advanced membrane
- Higher temperature is expected to result in additional performance improvement, with testing planned for the remainder of the fiscal year
- Future work should include design and operation of an integrated system

Technical Back-Up Slides

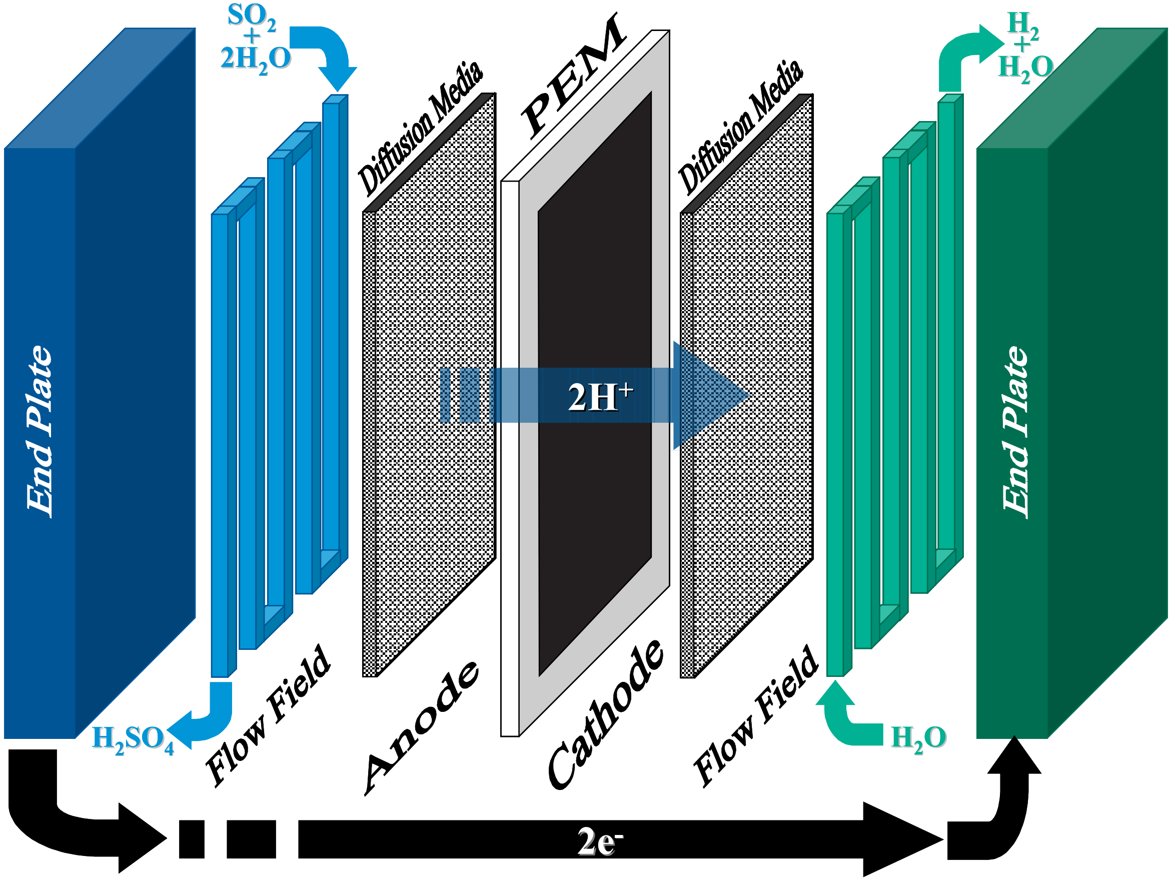
SO_2-Depolarized Electrolyzer (SDE) Concept

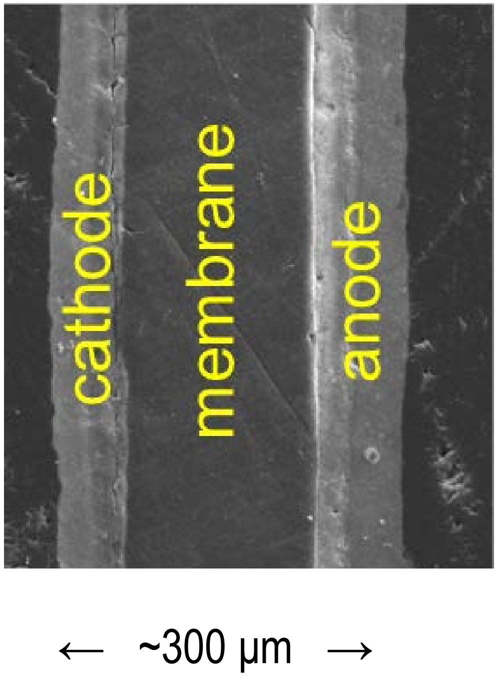
SO_2-Depolarized Electrolyzer based on Proton Exchange Membrane (PEM) Design



- SO_2 oxidized at the anode to form H_2SO_4 and H^+ ions; hydrogen formed at cathode
- Reversible cell potential reduced by 87% vs water electrolysis (0.16 V vs. 1.23 V); practical cell voltage of 0.5 to 0.6 V targeted
- PEM cell design concept permits more compact arrangement, reduced footprint, and lower cost versus earlier parallel plate designs
- PEM design leverages extensive R&D and advances being done for PEM fuel cells by auto companies and others
- Performance Goal: 600 mV at 500 mA/cm^2 by 2020 and longer-term goal of 500 mV to achieve MYRDD H_2 cost targets.

PEM Electrolyzer Design Concept



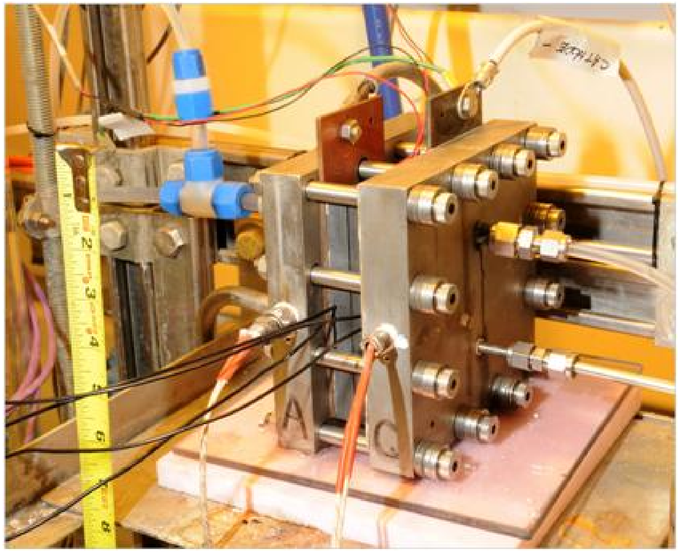


MEA Cross-section

Electrolyzer Development and Testing

Prior Single Cell Test Facility 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 of 10-20 liters per hour
- Over 40 MEA designs tested
- 1000 hour continuous operation achieved



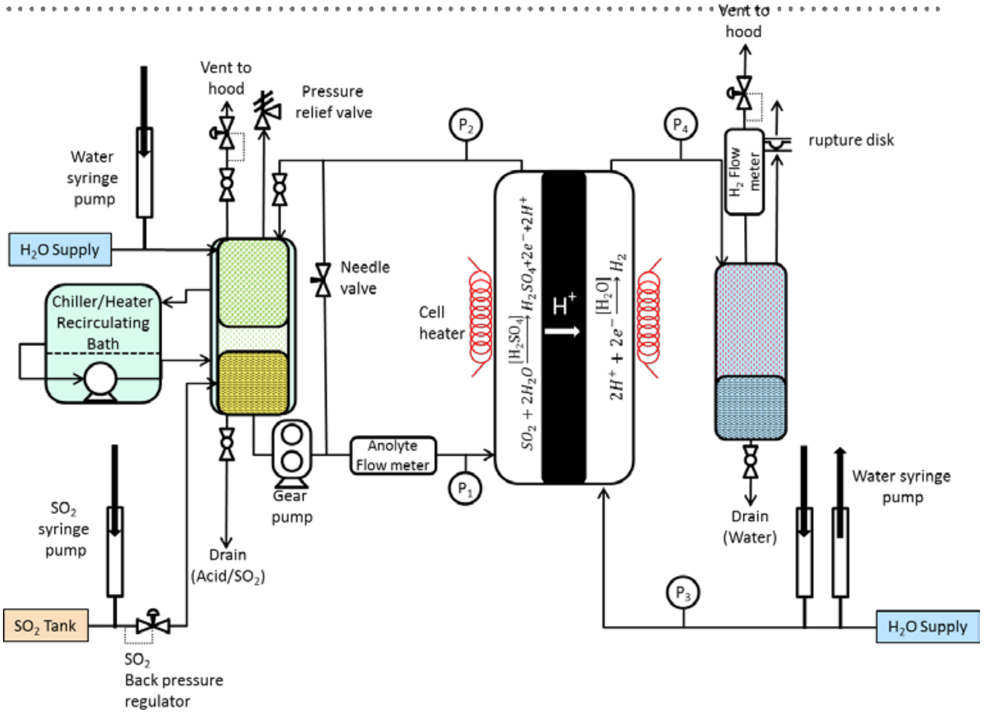
Single Cell Electrolyzer and Test Facility

New Versatile Test Facility Required

- Previous SDE testing performed in atmospheric button cells and larger Single Cell Test Facility
- Facility limited to 80°C cell operating temperature
- Smaller, more versatile test facility capable of higher temperature and pressure operation was required
- New Pressurized Button Cell Test Facility (PBCTF) was designed and constructed to test advanced high-temperature membranes

Pressurized Button Cell Test Facility (PBCTF)

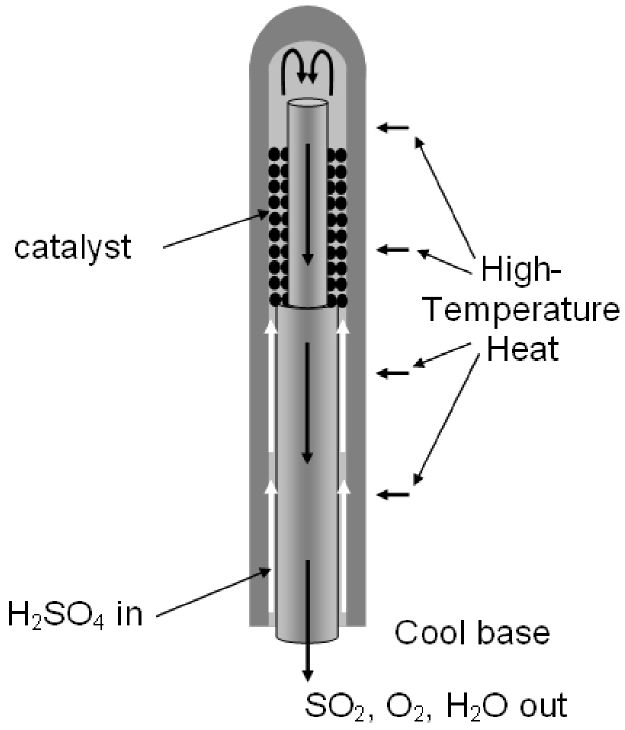
- Allows testing of electrolyzer components (membranes, catalysts, flow distributors) at high temperatures and pressures
  - *Prior button cell testing limits: 80°C and atmospheric pressure*
  - *Target higher performance: 130°C and 10 atm*
- Requires more complex system to recirculate highly corrosive sulfuric acid, saturate anolyte with sulfur dioxide, and remove acid and hydrogen products



- System consists of pumps, tanks, flow-meters, pressure transducers, heaters, fittings, and electronic components to allow automated operation
  - *Material construction requires the use of polymer lining on steel parts where possible, while metal wetted parts are made of tantalum and zirconium in order to avoid corrosion failure*
  - *Off-the-shelf components that can not handle the chemistry have to be custom fabricated*
  - *Corrosion resistant anolyte pump in small size is particularly demanding*

Step 2: Acid Vaporization and Decomposition

- **Sulfuric acid decomposition represents the thermal step in the Sulfur Cycle**
- **Requires high-temperature heat input in the range of 500-900°C**
- **Innovative vaporizer/decomposer was designed and successfully demonstrated by Sandia National Laboratory under NHI program**
- **Optimizing heat input for acid concentration and acid decomposition is key to high process thermal efficiency**
- **SRNL has optimized overall HyS flowsheet to provide high efficiency under realistic commercial operating conditions (cost estimates performed with industry partners)**



Sandia Bayonet Decomposer