Electrolyzer Component Development for the HyS Thermochemical Cycle

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Project PD096

Overview

Timeline

- Project Start Date: May, 2013
- Project End Date: September 30, 2017*

Budget

FY14 DOE Funding: $85,000

FY15 Planned DOE funding: $415,000

Total DOE funding thru FY15: $800,000

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

Cost Share Percentage: 3%

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
- Partners: University of South Carolina, German Aerospace Center (DLR)
- Prior work included numerous other industry and university partners, including Air Products and Chemicals, Westinghouse, Shaw, PBMR, SNL, DuPont, Case Western Reserve Univ., Clemson Univ., Vanderbilt Univ., Giner Electrochemical

*Project continuation and direction determined annually by DOE.

Project Objectives

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

Fiscal Year 2015 Objectives

- Identify design options for a solar-heated HyS process, including consideration of both thermal energy storage and chemical energy storage
- Perform system design and analysis, develop Aspen Plus™ process flowsheet models, material and energy balances and calculated plant performance and efficiency
- Estimate capital costs for a commercial plant and utilize the H2A analysis tool to determine projected hydrogen production costs for various design and operating scenarios
- Develop technical solutions to improving the performance, lifetime and cost effectiveness of the SDE, including identification of improved electrocatalysts and characterization of at least three candidate high temperature proton-exchange membranes
- Construct and operate a pressurized button cell test facility (PBCTF) and demonstrate high temperature, high pressure SDE operation using advanced membranes with at least a 50 mV improvement over performance with the baseline Nafion® PEM

Relevance – Addressing Technical Barriers

Coupling Concentrated Solar Energy and Thermochemical Cycles (Barrier T)

- Prior HyS process designs were based on nuclear heat and continuous operation
- Innovative designs have been developed considering various solar receiver approaches, thermal and chemical energy storage, integrated and non-integrated operation of the two major process reactions, and optimization of heat integration for high thermal efficiency

Materials and Catalyst Development (Barrier W)

- Improved electrocatalysts for the SO_2-depolarized electrolyzer were identified and will be tested in MEAs using the new PBCTF
- PBCTF operation was initiated and baseline Nafion® membranes characterized. Higher temperature membranes permitting improved performance have been identified and samples obtained. These will be incorporated into MEAs and tested later in the year

Chemical Reactor Development and Capital Costs (Barrier X)

- Electrolyzer (SDE) development and optimization of the HyS solar system design will enable meeting DOE hydrogen production goals based on solar thermochemical technology

Approach - Build on prior work for the Hybrid Sulfur Process

- Hybrid Sulfur (HyS) is a two-step process based on sulfur oxidation and reduction
- Initial work was done by Westinghouse Electric in the 1970's and 1980's
- SRNL led HyS development program for the DOE Nuclear office from 2005-2010
- Key Step in HyS Cycle is electrochemical water-splitting based on use of an SO_2 depolarized electrolyzer (SDE)
- SRNL developed a PEM-based SDE using Nafion® membranes and Pt catalyst
- Button-cell testing was performed on various cell membranes at atmospheric pressure
- Single cell testing at 60 cm^2 was performed at 80°C and 6 atm; a 1000 hour continuous run was demonstrated
- Higher temperature operation with improved catalysts & membranes were identified as a key future improvements

Hybrid Sulfur Chemistry

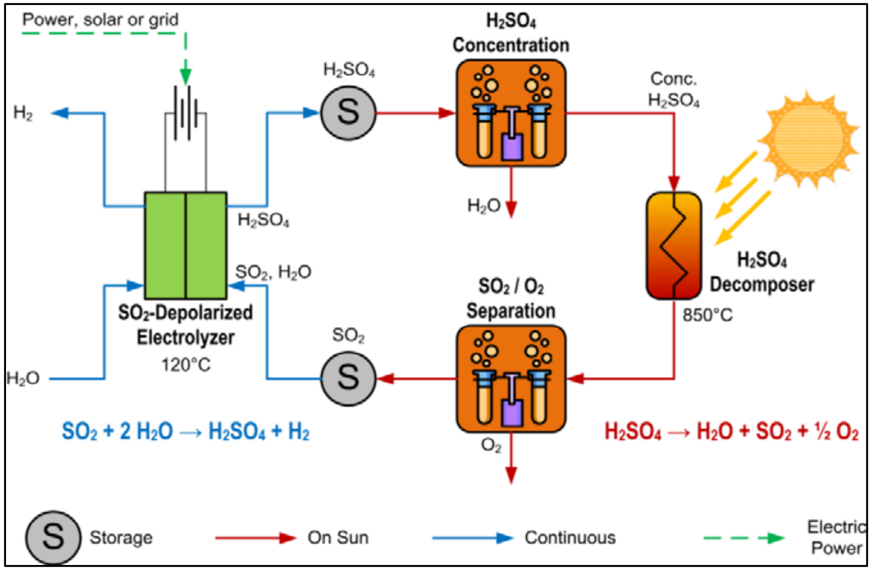
$$H_2SO_4 \leftrightarrow H_2O + SO_2 + \tfrac{1}{2}\,O_2$$

(thermochemical; 800-900 °C)

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

(electrochemical; 80-120 °C)

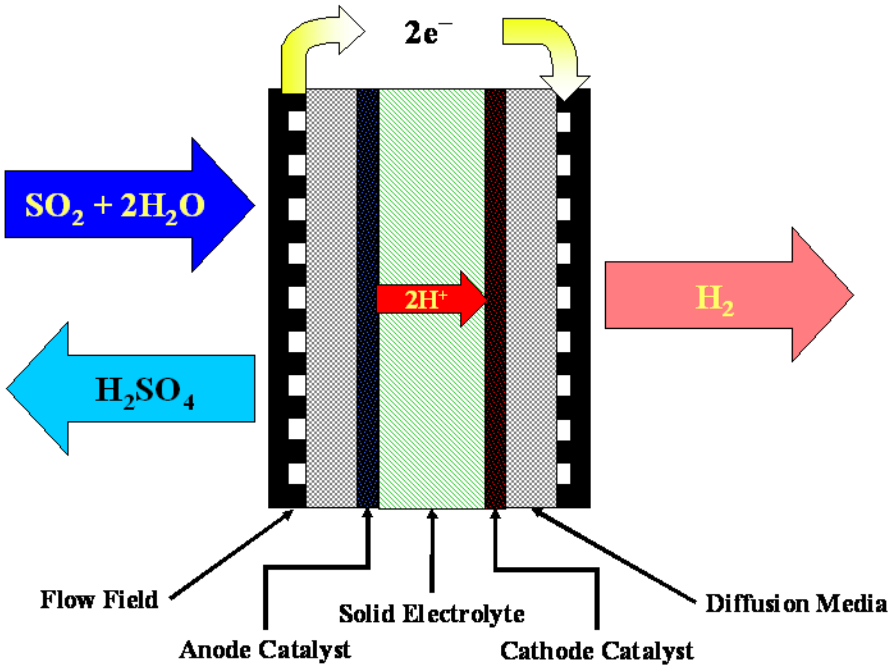
Net Reaction: $H_2O \rightarrow H_2 + \tfrac{1}{2}\,O_2$



Solar HyS Process Schematic

Approach – SO_2-Depolarized Electrolyzer (SDE) Concept

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



- SO_2 is oxidized at the anode to form H_2SO_4 and hydrogen ions
- Hydrogen is formed at cathode
- Reversible cell potential is reduced by 87% vs water electrolysis (0.16 V vs. 1.23 V)
- Practical cell voltage of 0.5 to 0.6 V compares with 1.6-2.0 V for water electrolysis
- Requires efficient high temperature thermal step to regenerate SO_2 and close the cycle
- 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 H2 cost targets.

Approach – Technical Efforts Focus on Two Main Tasks

Task 1. System Design and Analysis

- Most previous HyS system designs were based on continuous operation using nuclear heat; diurnal solar operation requires process changes and a means for energy storage
- Various power tower concepts, thermal energy storage and chemical energy storage, direct and indirect heating of the high temperature acid decomposer, and integrated and non-integrated operation of the two major process sections will be analyzed
- Complete Aspen Plus™ flowsheets and a detailed system performance will be prepared. Capital costs will be estimated and an H2A analysis of resulting hydrogen production cost prepared

Task 2. Electrolyzer Development and Testing

- Losses due to oxidation kinetics at anode represent 70% of total SDE overpotential; this will be addressed by higher temperature operation and development of improved electrocatalysts
- Advanced PEMs capable of operation with sulfuric acid at ≥120°C and 5 atm will identified: University of South Carolina will collaborate in development of polybenzimidazole (PBI) membrane
- A high temperature, high pressure button cell test facility will be constructed and commissioned to permit rapid evaluation of design options; challenges include high P and T and need to saturate sulfuric acid with SO_2 and recirculate the highly corrosive acid solution (i.e. special materials)
- Improvement in cell voltage of >50 mV versus baseline Nafion® design is targeted in first year

Milestone 1. Baseline SDE Operation

Establish baseline SDE performance with a Nafion® PEM. Identify at least three high temperature PEM candidates capable of ≥120°C and 500 kPa. Due: 12/31/14 Status: Complete

Milestone 2. Develop Baseline Solar HyS Design and Reference Performance

Develop Solar HyS process design including Aspen Plus™ flowsheet and overall system performance evaluation. Due: 3/31/15 Status: Complete

Milestone 3. Characterize MEA Performance at High Temperature

Characterize MEA performance at ≥120°C for at least three high temperature PEM candidates and determine their potential to reduce cell polarization by ≥100 mV versus baseline Nafion® membrane. Due: 6/30/15 Status: On Schedule

Milestone 4. Solar HyS Conceptual Design and H2A

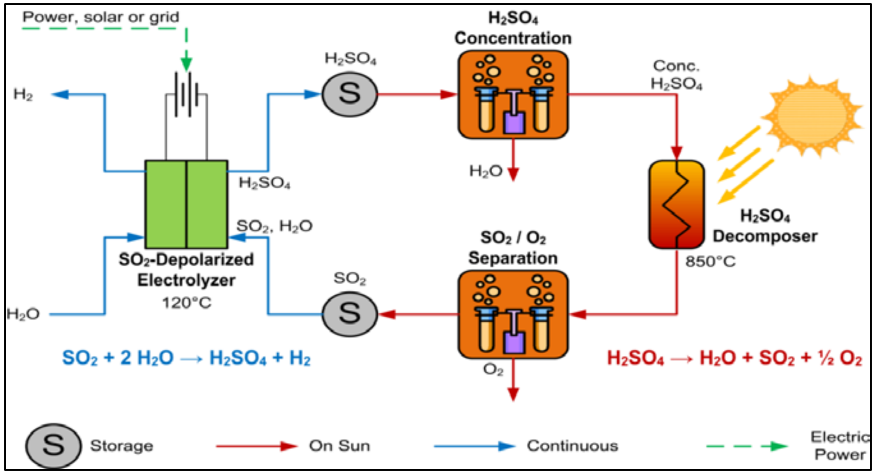
Issue conceptual design report including optimized system design, flowsheet, performance, cost estimates and H2A analysis for Solar HyS. Due: 9/30/15 Status: On Schedule

Go/No-Go Decision (9/30/2015)

Demonstrate MEA performance for a high-temperature membrane that achieves ≥50 mV lower cell voltage than baseline Nafion® . This is first step toward longer range goal of ≥100 mV goal.

Accomplishments – System Design and Analysis

Flowsheet analyses and tradeoff studies have identified preferred HyS system design options



Alternative Flowsheet Configurations

- Gaseous-fed or liquid-fed electrolyzer
- Continuous or diurnal operation
- Thermal versus chemical energy storage
- Use of a secondary heat transfer fluid
- Integrated or separate operation of process sections (electrolysis and acid decomposition)

Vapor fed vs. liquid fed SDE

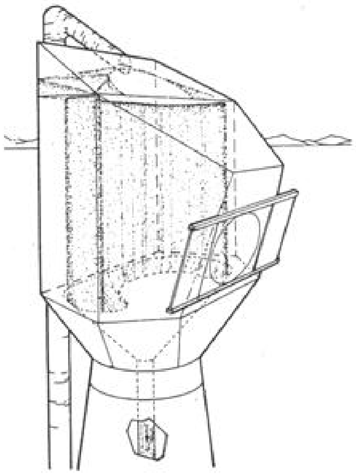
- SO_2-depolarized electrolyzer can be operated with anode feed consisting of either vapor (SO_2 and H_2O) or liquid (SO_2 dissolved in sulfuric acid); both result in liquid H_2SO_4 anode product
- Previous testing showed similar SDE performance for the two options, but they require different flowsheet designs to close the cycle and integrate the SDE with the solar acid decomposer
- Flowsheet analysis and trade studies indicate that the liquid feed approach is preferred
  - *Vapor feed simplifies prototype SDE testing, but results in a more complex anode flow path for closed cycle operation of the complete HyS flowsheet*
  - *Vapor feed requires phase change (vapor feed to liquid product), greatly increasing the magnitude of heat removal from SDE and reducing overall system efficiency*
  - *Water vapor pressure limits feasible SDE operating pressure and allowable SO_2 conversion*

Accomplishments – Solar HyS Process Design Options

Solar receiver design will dictate preferred HyS process configuration

Solar Receiver Options

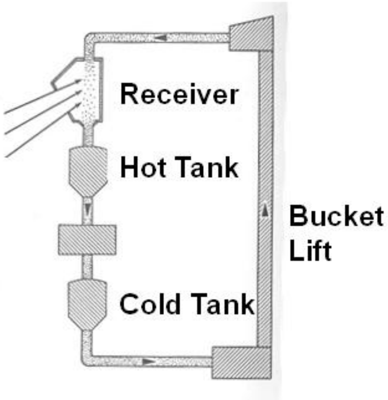
- Falling Particle Receiver (Sandia National Laboratory)
  - Uses heated “sand” for thermal energy storage
- Cavity receiver with tubular heat exchanger (Brayton Energy)
  - Secondary heat transfer fluid (e.g. He) heated in receiver
- Direct solar-heated acid vaporizer and decomposer (DLR)



SNL Falling Particle Receiver

DLR 100 kW Solar H_2 Receiver

CSP Test Facility at Sandia



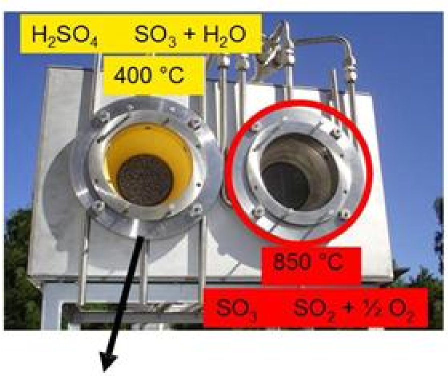
Receiver/Storage Concept

Accomplishments – Solar HyS Process Design Options

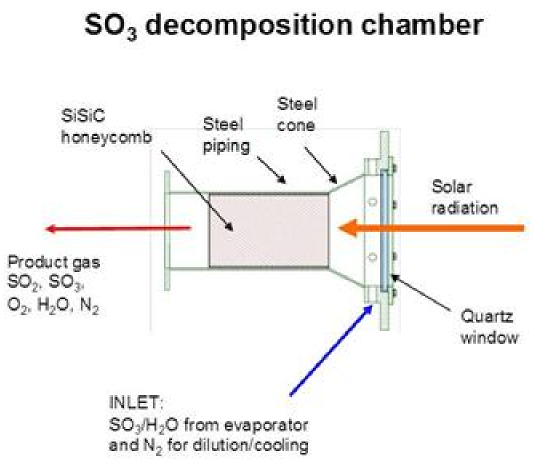
Bayonet acid decomposer and thermal energy storage selected for baseline flowsheet

- Direct solar-heating of acid decomposer (DLR) requires diurnal operation and chemical storage of wet liquid SO_2 (under pressure) and sulfurous acid (SO_2-saturated water)
- Bayonet Acid Decomposer (developed during earlier NE program) requires indirect heating using a heat transfer fluid (Brayton Energy receiver) or hot sand (Falling Particle Receiver)
- Falling Particle Receiver (FPR) permits continuous operation with thermal energy storage
- Tradeoff studies established FPR and Bayonet Decomposer as baseline selections

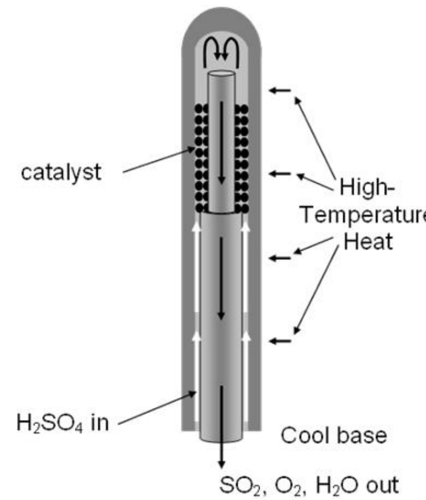
DLR Direct Solar-Heated Acid Decomposer



Model of evaporator presented by Haussener, et al. at ASME Conference, Puerto Rico, 2012



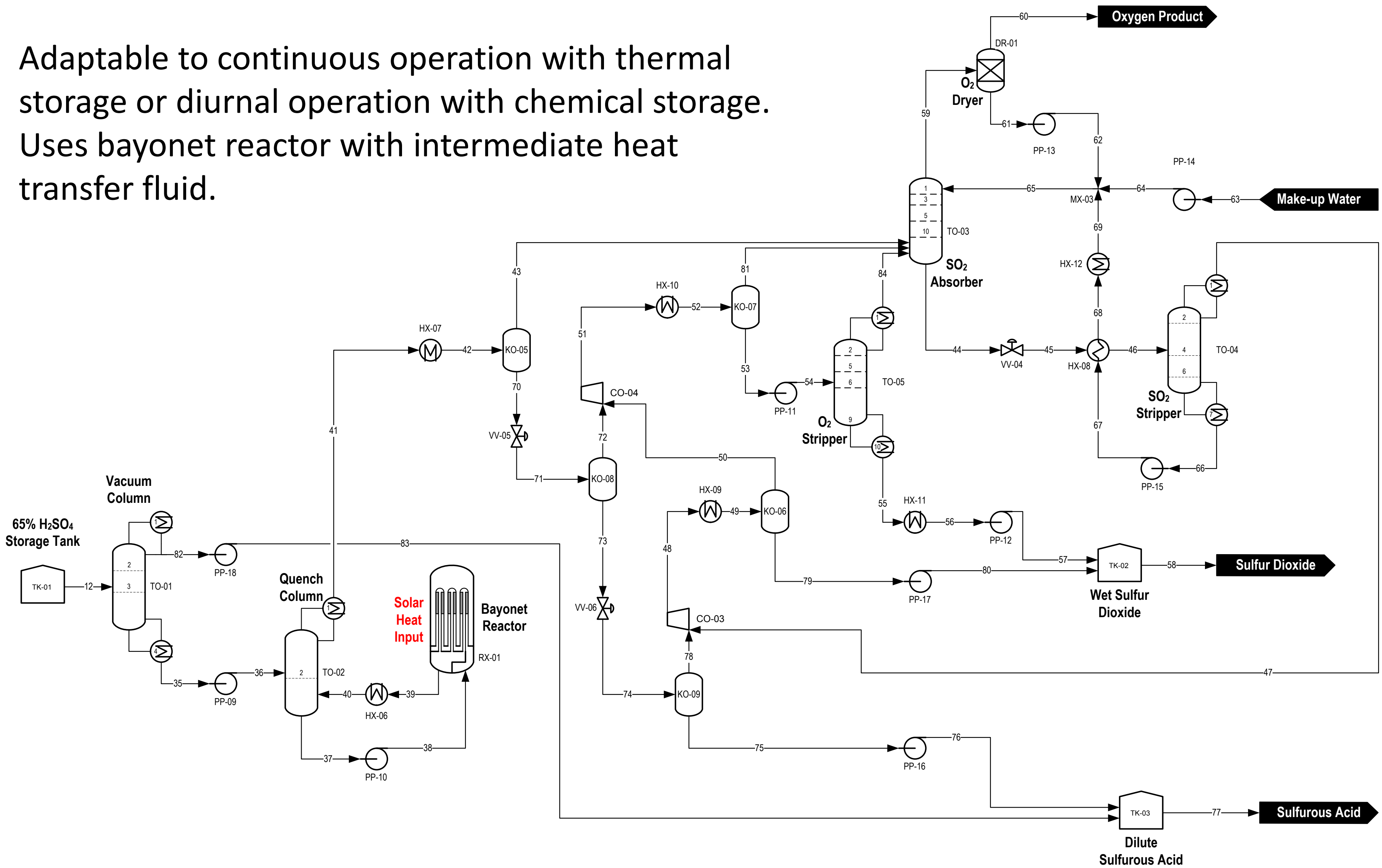
Noglik, et al., International Journal of Energy Research, 2011



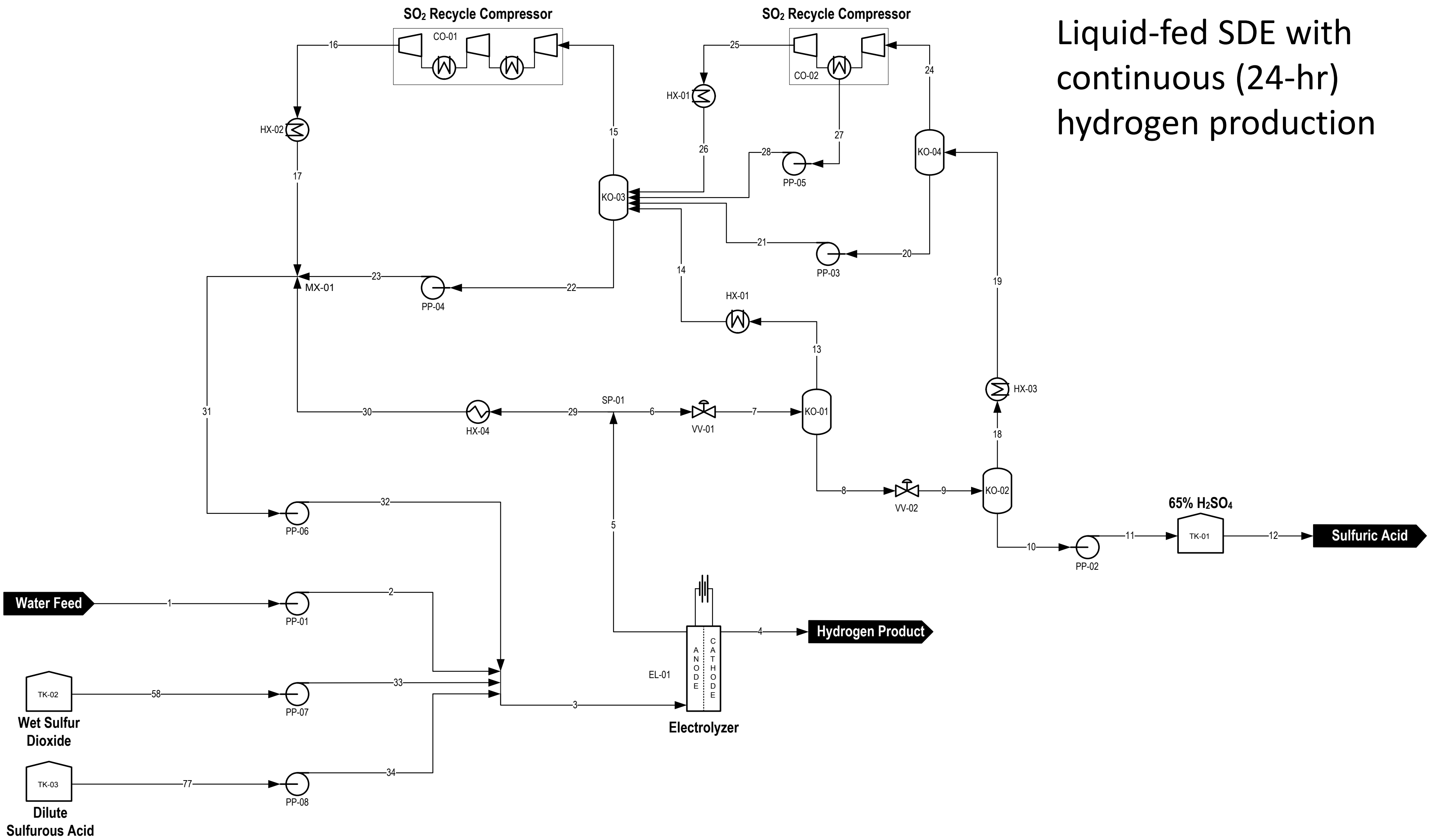
SNL Bayonet Acid Decomposer

Accomplishments – Baseline Solar HyS Acid Decomposition Flowsheet

Adaptable to continuous operation with thermal storage or diurnal operation with chemical storage. Uses bayonet reactor with intermediate heat transfer fluid.



Accomplishments – Baseline Solar HyS Flowsheet (Electrolyzer Section)



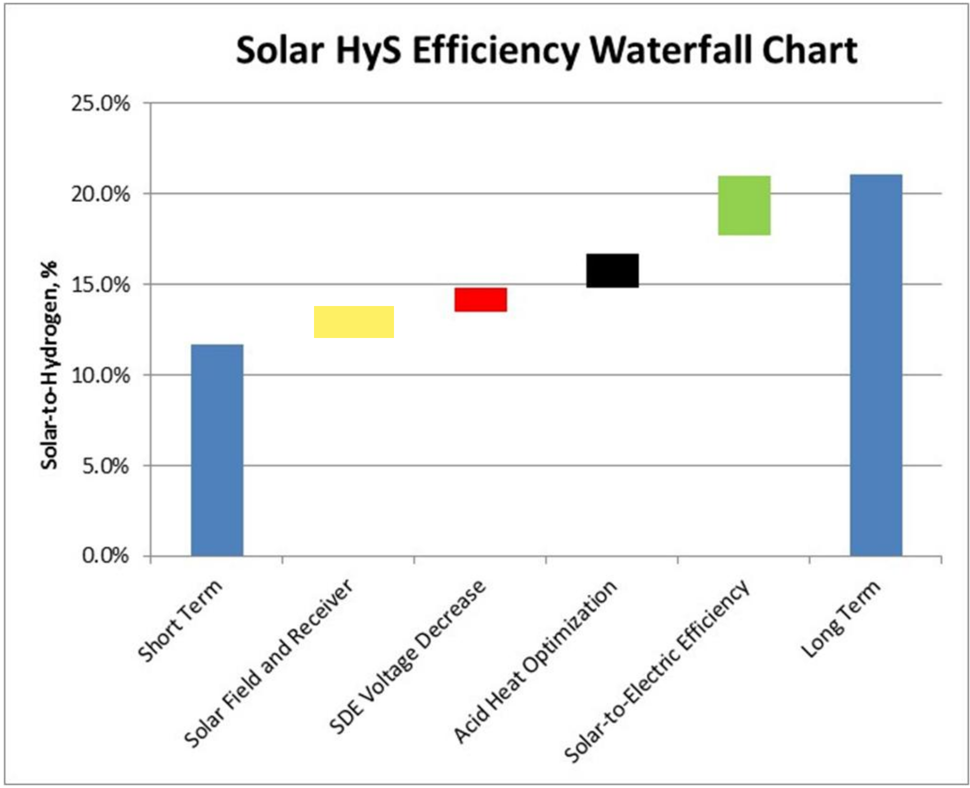
Liquid-fed SDE with continuous (24-hr) hydrogen production

Accomplishments – Baseline Solar HyS Design and Performance

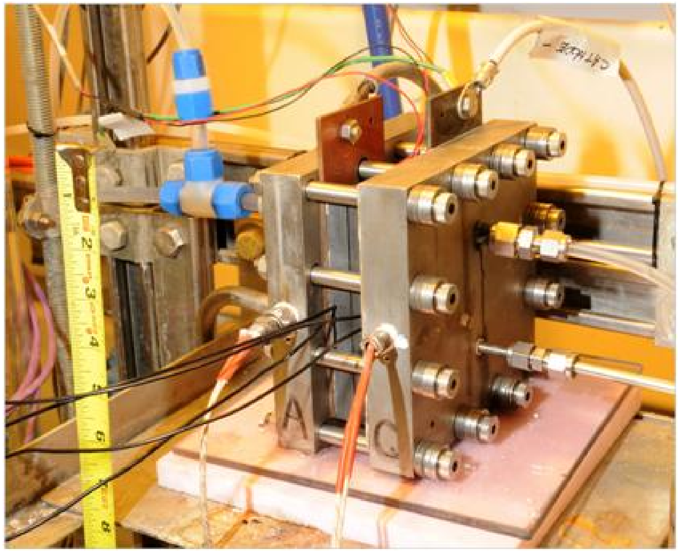
- Projected energy efficiency exceeds MYRRD 2020 goal of 20.0%
- Near Term to Long Term gains require improvements in both solar system and HyS process (lower SDE voltage and further process heat optimization)

Solar HyS Efficiency Assumptions

Plant Section	Near Term Energy Efficiency	Future Energy Efficiency
Heliostat Field	45%	55%
Solar Receiver	85%	90%
Thermal Energy Storage	95%	95%
Solar Electric Generation	15%	22%
SDE Electrolyzer	600 mV	500 mV
Thermal Input to Acid	477 kJ/mol	342 kJ/mol
Solar Input for Electricity	829 kJ/mol	460 kJ/mol
Solar Input for Heat	1247 kJ/mol	691 kJ/mol
Solar-to-Hydrogen Conversion Ratio	**11.7%**	**21.0%**



Accomplishments - Electrolyzer Development and Testing



New Versatile Test Facility Required

- Previous SDE testing performed in atmospheric button cells and larger Single Cell Test Facility
- Facility limited to 80ºC 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

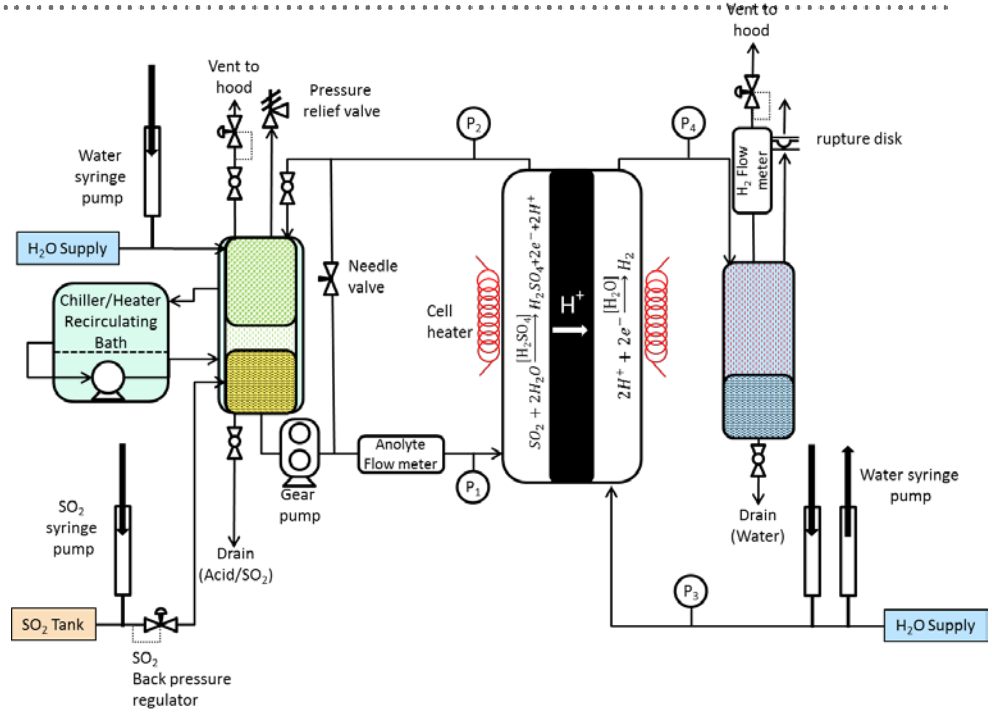
Single Cell Electrolyzer and Test Facility

<u>Prior Single Cell Test Facility Capabilities</u>

- **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**

Accomplishments – 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 atmospheres*
- 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*

Accomplishments – Status of Pressurized Button Cell Test Facility

PBCTF is complete and operational. Characterization of baseline Nafion® MEA is in progress.

- Final assembly and programming of the PBCTF was completed
- Final safety approval of the pressure section was received after major delays due to SRNL safety protection backlog
- MEAs using Nafion membrane were prepared and tested at temperatures up to 90°C
- An anolyte pump capable of higher temperature operation (130°C) is on order and will be used after lower temperature characterization is completed

Accomplishments – Button Cell Flow field modification

Radial flow field design is being optimized

Previous Work (60 cm^2 rectangular cell)

- Work in the larger cell resulted in proof of concept of long term stable performance (1000 hour continuous operation)
- Flow field consisted of larger interdigitated design
- Low pressure drops and good flow distribution

60 cm^2 cell

Small cell (2 cm^2 circular cell)

- Anolyte flows a similar distance between inlet and outlet as larger interdigitated design, but radial design results in poorer flow distribution
- Pressure drop arises from the radial distribution of the new cell vs. linear distribution of flow in previous cell
- New concentric radial flow field being fabricated

2 cm^2 cell

Accomplishments – Pressure and Temperature Effect

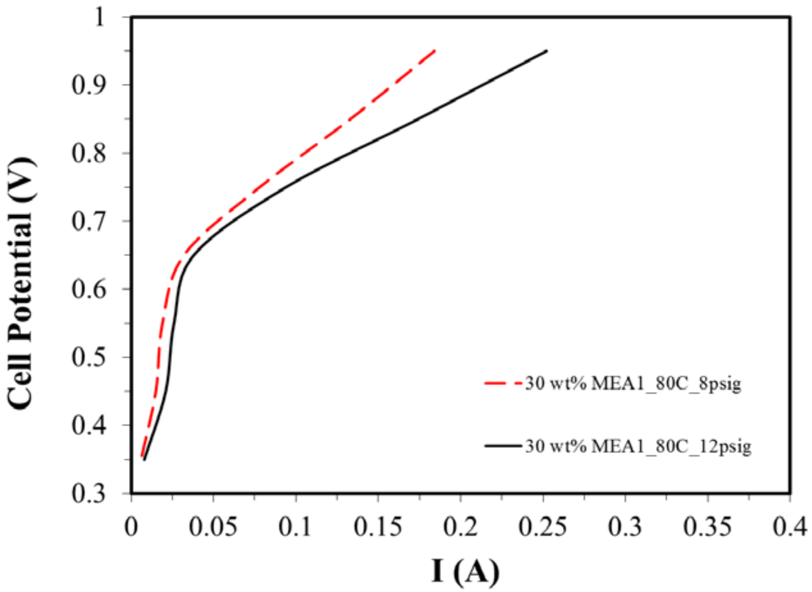
PBCTF demonstrates pressure and temperature effects on SDE performance. Further cell design optimization is required.

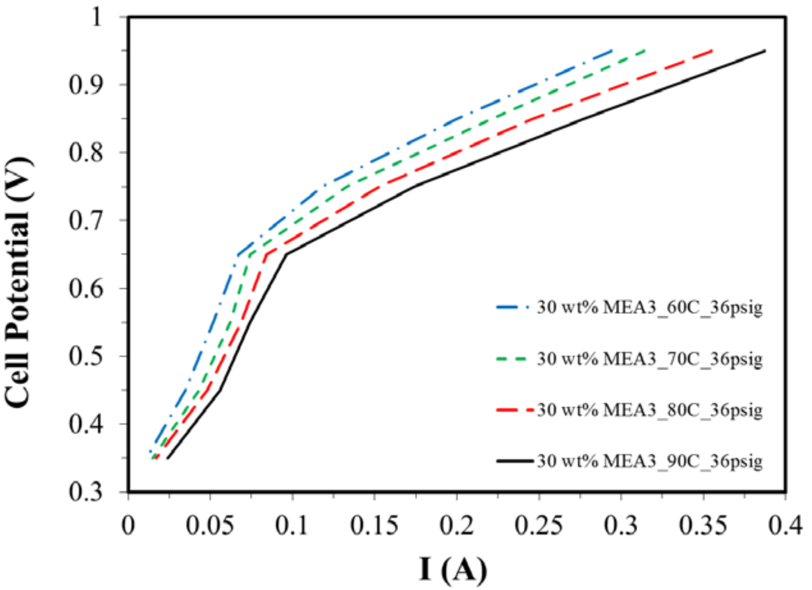
Pressure Effect

- Pressure determines the concentration of SO_2 in the anolyte
  - *Data shows SO_2 limited operation*
  - *Previous cell design operated at lower pressures to improve stability over time*
- Data shows flow field has to be optimized

Temperature Effect

- Temperature effect on the kinetics can be observed
- Higher temperatures result in higher currents
- Use of higher temperature operation membranes should result in higher performance (lower cell voltage)

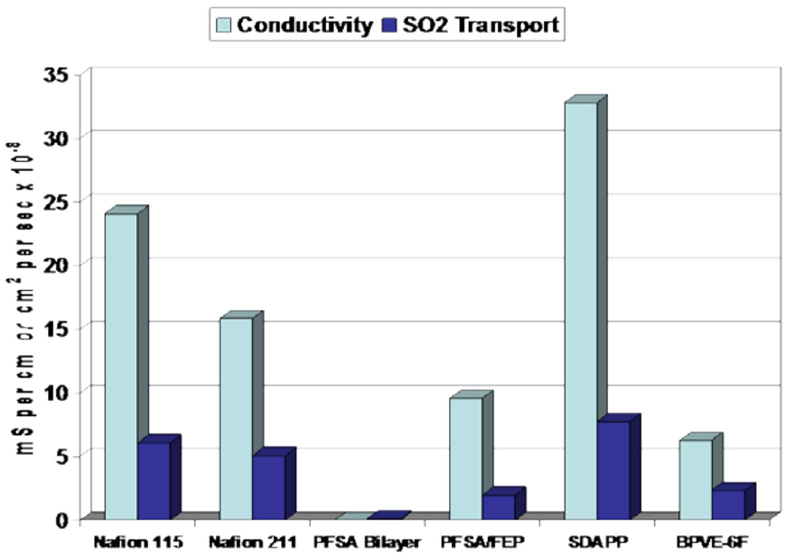




Accomplishments – Performance Testing of Advanced MEAs

Candidate high temperature membranes have been identified and MEA fab is underway

- **Goals and significance**
  - Higher temperature membranes offer several major benefits versus Nafion PEM:
    - *Faster anode kinetics due to increased temperature*
    - *Improved ionic conductivity*
    - *Elimination or reduction in sulfur crossover*
    - *Operation with stronger acid concentrations*
  - Several high temperature membranes were tested under earlier NE program, but testing was limited to low T and P due to test facility limitations
- **Selection of high temperature membranes**
  - Three membrane candidates have been identified
    - *Sulfornated Polybenzimidazole (s-PBI) – USC*
    - *Sulfonated-diels-alder poly phenylene – SNL*
    - *Sulfonated PFCB – BPVE – Tetramer Technologies/Clemson University*
  - Other high temperature membranes being sought



Previous HT membrane results at 60°C and 1 atm

Accomplishments – Responses to Previous Year Reviewers' Comments

"The work presented has been focused on the electrolyzer, but the interface with the solar heat is also important and has not yet been considered in any detail."

"The project should begin studying/modeling an interface with solar heat."

- Due to funding restrictions, FY14 tasks were limited to electrolyzer development only, since this was considered the most critical issue. FY15 program has been expanded to include a System Design and Analysis task with major focus on the solar interface, including collaboration with the European solar hydrogen program at DLR (Germany).

"Questions were raised at the review about the stability of PBI and should be addressed"

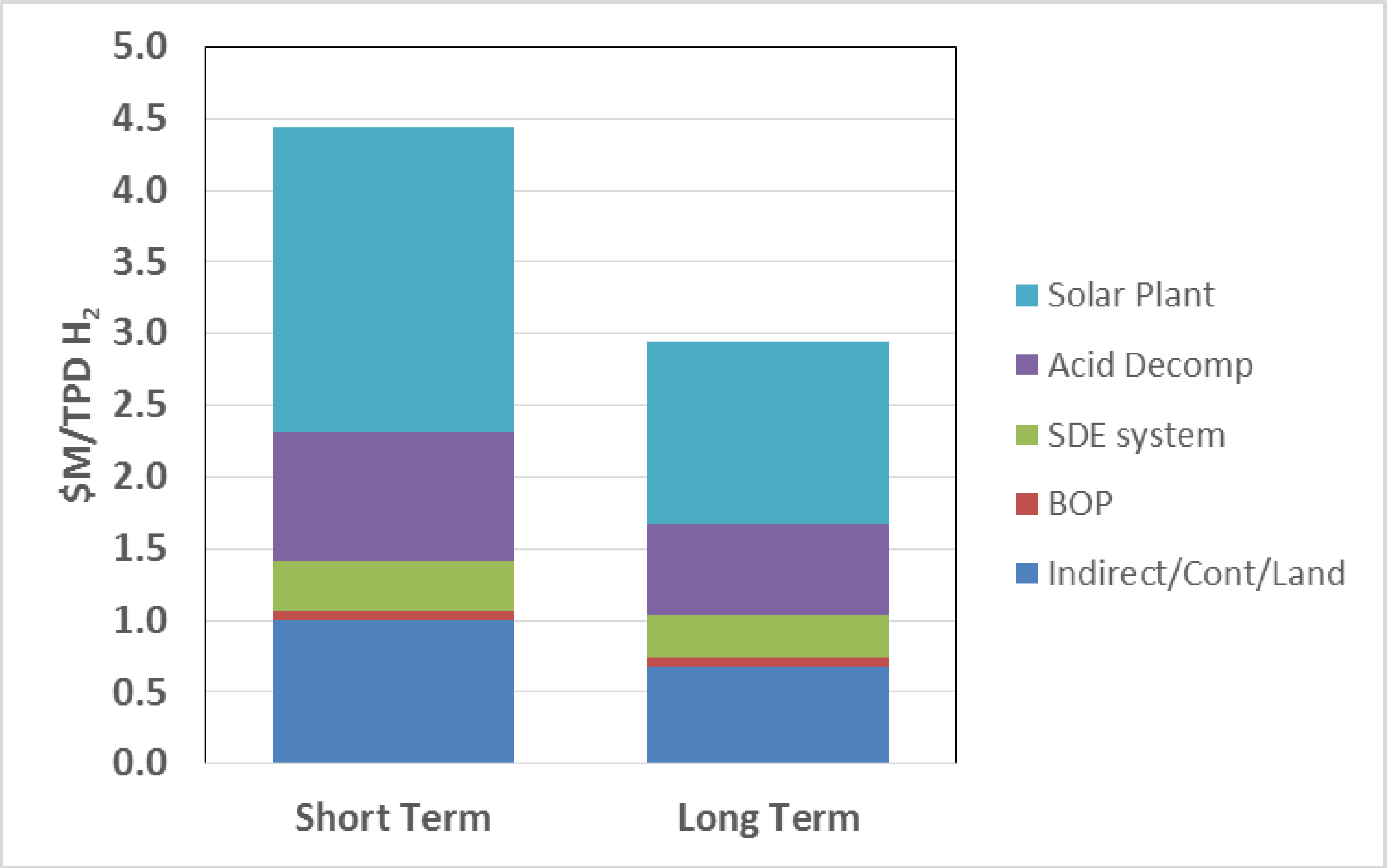
- USC is developing s-PBI membranes for the specific SDE application. They believe the new PBI membranes will overcome stability problems associated with earlier PBI fuel cell membranes. SRNL has also identified two other high temperature membranes and will continue to search for additional candidates to be tested in the PBCTF.

"An analysis using the H2A should have been included in this work."

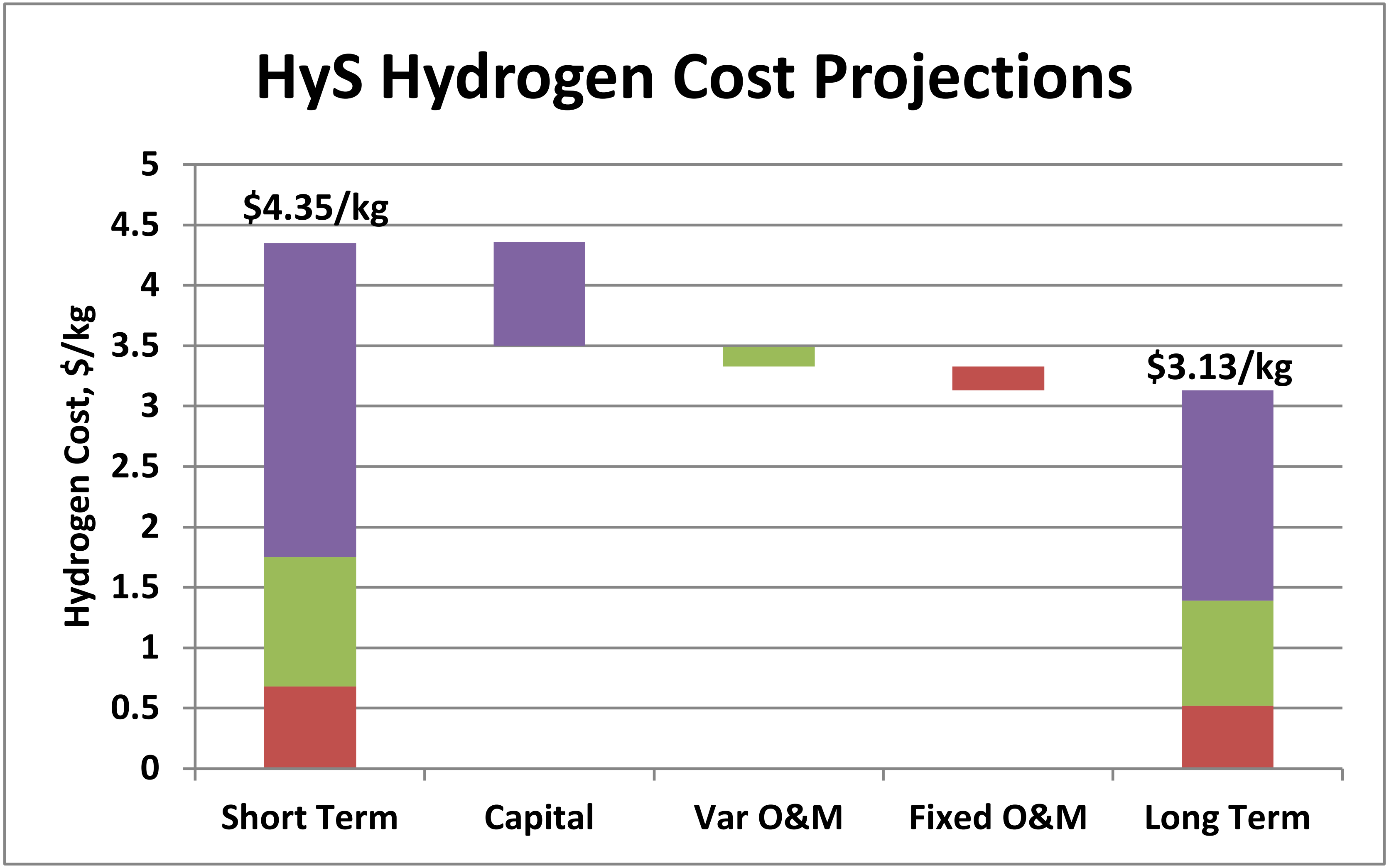
"The process is interesting, but it is not clear that a low hydrogen price can be achieved because it combines solar and electrolysis."

- Significant effort in FY15 is being devoted to optimizing the HyS integration with solar heat. Detailed flowsheeting, cost estimates and H2A analysis are planned. Initial results show that the process can meet the MYRDD cost and efficiency goals (see next slide)

Baseline Solar HyS Plant Investment Costs



Baseline HyS Plant Waterfall Chart for Hydrogen Production Cost



Collaborations

- **University of South Carolina**
  - SRNL has collaborated with Dr. John Weidner and his team at USC for SDE development since 2005. USC is self-funded and focused on testing of gaseous-fed SDE and cell modeling
  - Dr. Brian Benewicz at USC continues to conduct an internally-supported program to develop their sulfuric acid doped PBI membranes (s-PBI)
    - *Initial results on gas-fed cell showed superior results as compared to Nafion®*
    - *USC will provide SRNL with s-PBI membranes for fabrication of MEAs and testing with liquid anolyte feed (SO_2-saturated sulfuric acid) in the PBCTF*
  - USC recently awarded a $100,000 grant for development of SDE with s-PBI membrane
- **Advanced Membrane Developers**
  - SRNL has obtained membrane samples from Sandia NL and Tetramer Technologies/Clemson University. Other advanced membrane candidates are being sought.
- **German Aerospace Center (DLR)**
  - DLR is developing a solar reactor to directly heat the sulfuric acid vaporizer and decomposer; prototype testing in the multi-kW range is planned
  - Funding is from EU's HycycleS program; agreement to share information with SRNL has been obtained

Remaining Challenges and Barriers

- **Operation of PBCTF remains challenging and modifications are required to permit long-term testing at high temperature and pressure**
  - Modifications to current button cell flow field are in process
- **s-PBI membranes have not been tested with liquid-fed anolyte**
  - Need to measure performance and long-term performance stability
  - Alternative high temperature membranes are being investigated
- **Continued improvement in SDE performance needs to be demonstrated**
  - Demonstrate progress toward commercial performance goals
  - Determine voltage degradation rates for long-lifetime operation (>40,000 hrs)
- **Solar HyS system design needs to be optimized for cost and efficiency**
  - Trade-off studies and more detailed system analysis are required to select preferred solar tower design and process configuration
- **Scale-up and integrated lab-scale testing of full HyS cycle are next major development steps**

Future Work

Remainder of FY 2015

- Modify PBCTF and complete testing at ≤90°C with Nafion® MEAs
- Fabricate MEAs using advanced membranes and test at ≤90°C
- Install new pump and modify PBCTF for high temperature operation
- Characterize MEAs with advanced membranes and improved electrocatalysts
- Demonstrate ≥50 mV performance improvement versus Nafion® baseline
- Continue system design and analysis work and tradeoff studies
- Prepare conceptual design report including optimized system design, flowsheet, performance, cost estimates and H2A analysis for Solar HyS

Plans for FY 2016

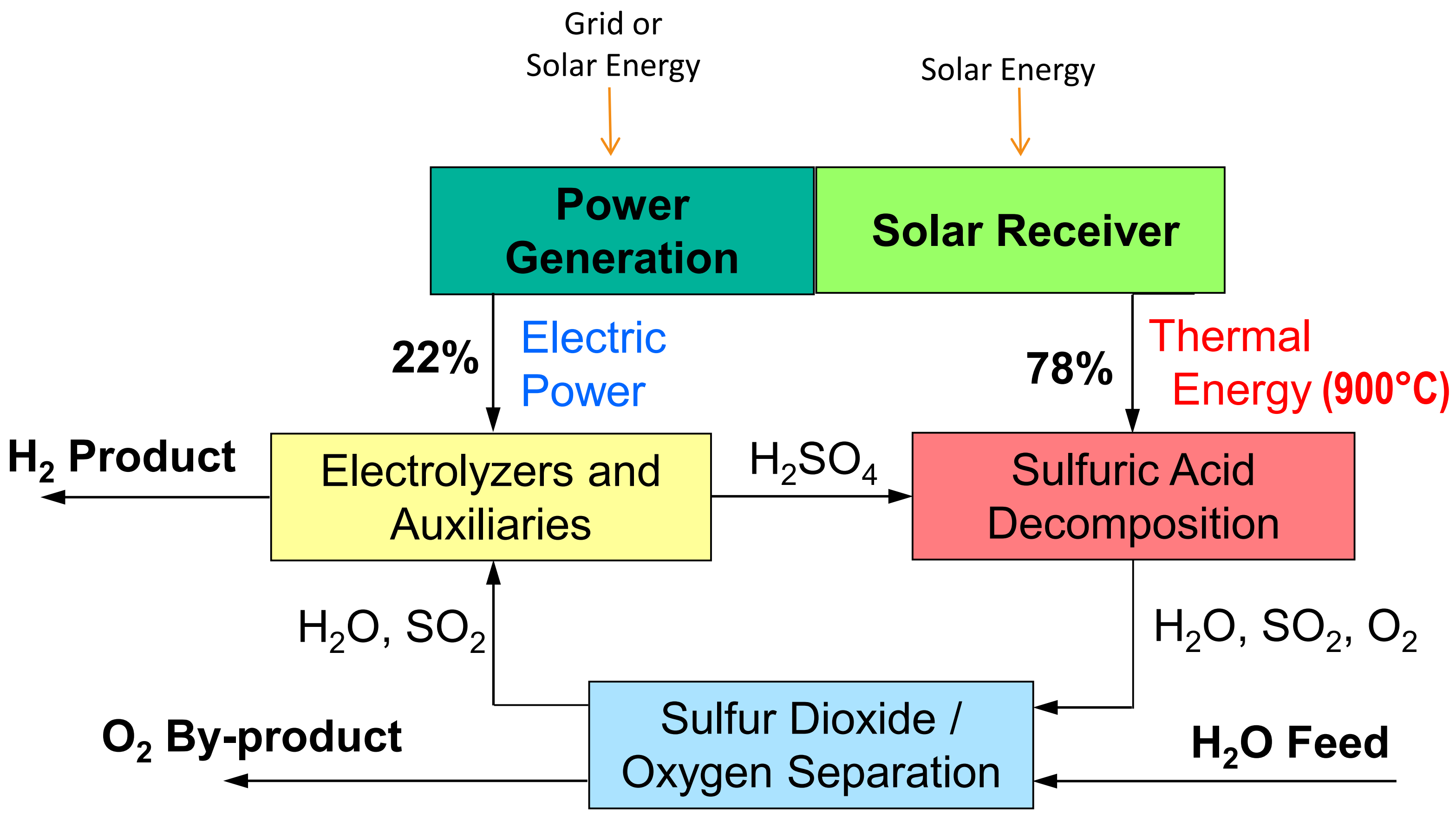
- Continue SDE development and testing
  - Demonstrate further voltage reductions with additional ≥50 mV improvement
  - Demonstrate long-term SDE performance stability with s-PBI or other high temp PEM
- Continue system design and analysis and Solar HyS process optimization
  - Conceptual design and cost estimates for major components
  - Analysis of Solar HyS performance changes as a function of seasonal changes

Project Summary

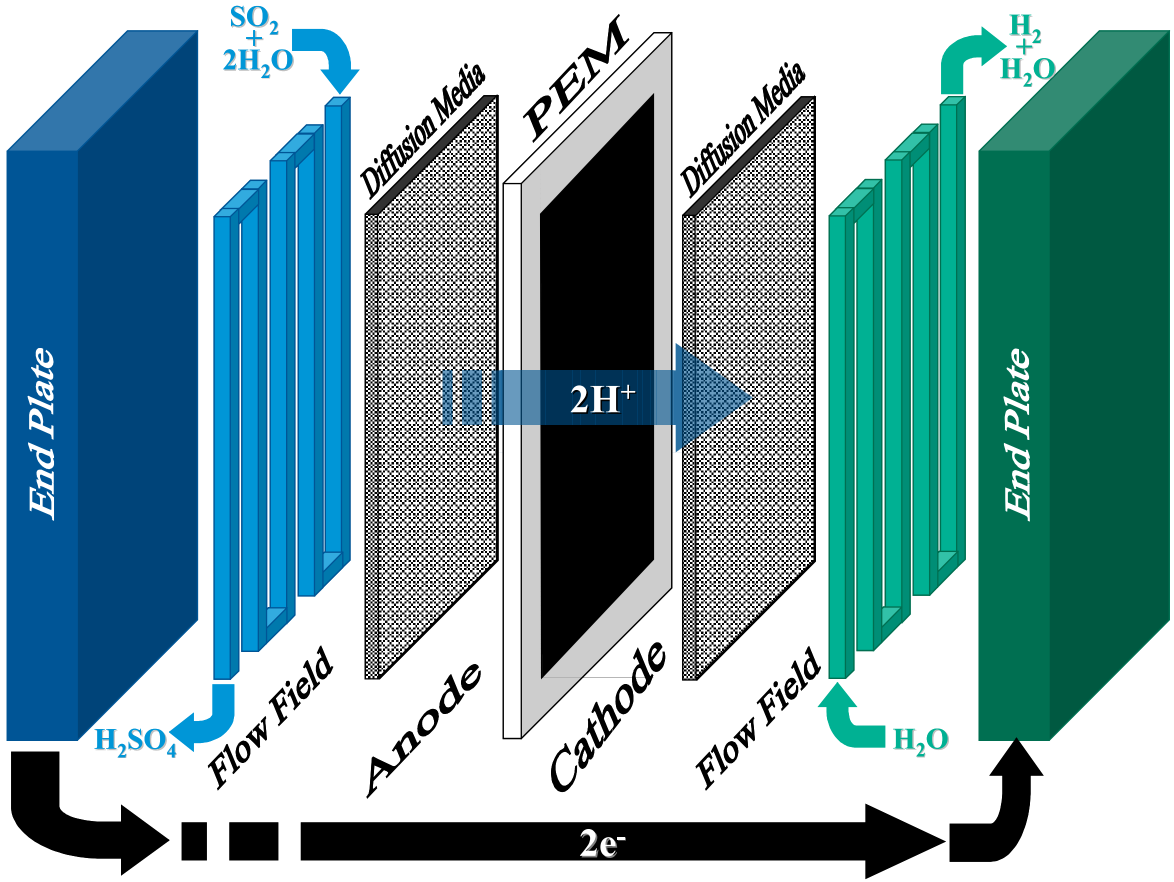
- ***Relevance*** HyS is the only all-fluid two-step thermochemical cycle and requires moderate (≤900°C) temperature. The SO_2-depolarized electrolyzer (SDE) is the key component for enabling cost-effective solar hydrogen production using the HyS process.
- ***Approach*** Utilize new PBCTF to evaluate electrocatalysts and advanced PEMs for the SDE operating at higher T&P to permit lower cell voltage (higher electrolysis efficiency) and produce more concentrated acid product (higher overall system efficiency). Conduct tradeoff studies and develop efficient Solar HyS flowsheet and system design.
- ***Technical Accomplishments*** 1) Developed efficient baseline Solar HyS flowsheets and conducted trade studies to identify solar receiver and system design options; 2) Initiated testing with PBCTF and tested baseline Nafion® MEAs; 3) Continued collaboration with USC to develop sulfonated polybenzimidazole membranes; 4) identified alternative high temperature membranes and established collaborations
- ***Future Work*** Fabricate MEAs using new catalysts and membranes and characterize performance using PBCTF. Complete system design and analysis studies and prepare optimized Solar HyS process design. Longer term, design and test integrated prototype of full HyS process.

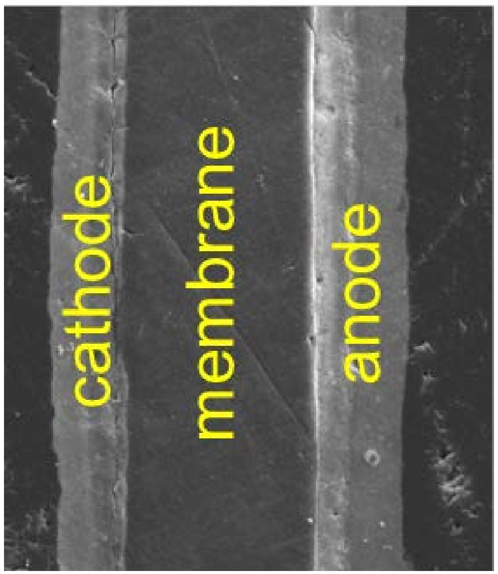
Technical Back-Up Slides

HyS Process Simplified Flowsheet



PEM Electrolyzer Design Concept





← ~300 µm →

MEA Cross-section

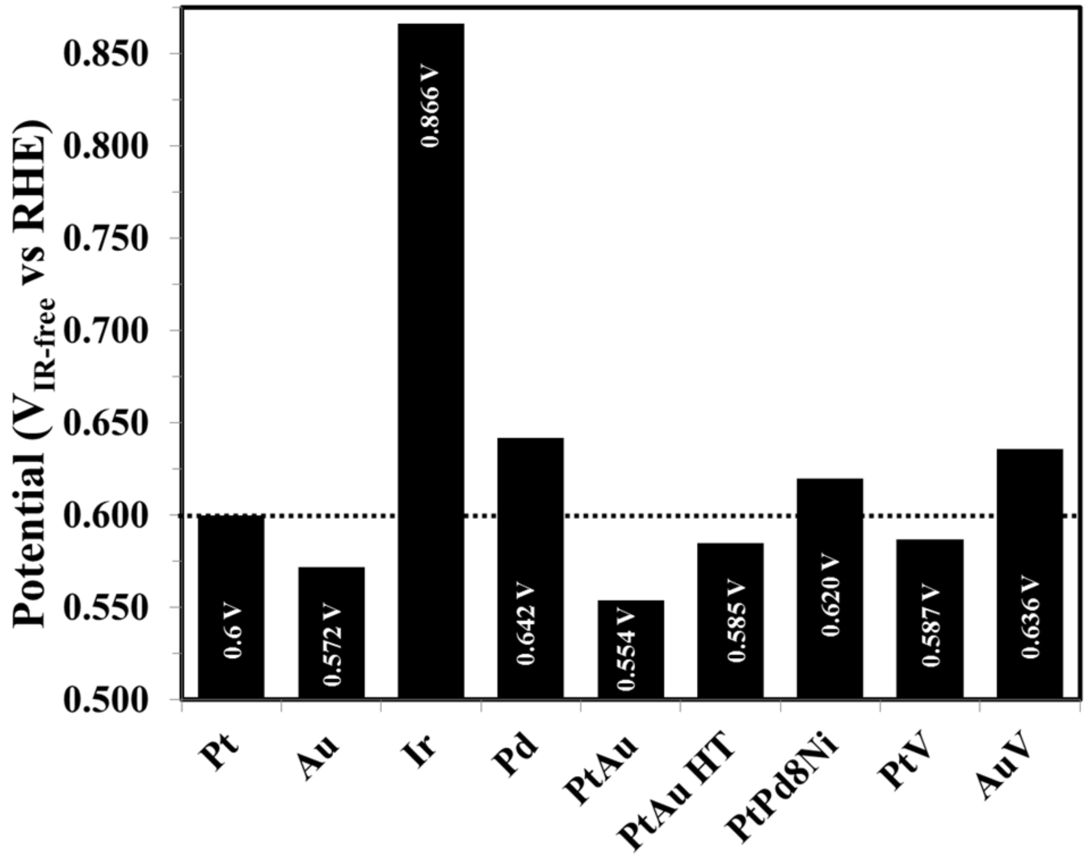
SRNL Progress under the DOE NHI Program

• SRNL Selected by NHI as HyS Lead Lab	2004
• Updated Conceptual Design of HyS Process	2005
• Proof-of-Concept for PEM-based SDE*	2005
• Pressurized, Elevated Temperature SDE Testing	2006
• Continuous 100-hour Longevity Test (DOE Level 1 milestone)	2007
• Testing of 100 lph H_2 Multi-cell Stack (DOE Level 1 milestone)	2008
• Electrolyzer Operation w/o sulfur build-up (DOE Level 1 milestone)	2009
• Plant Conceptual Design and Cost Estimate (Joint effort between SRNL & Industry)	2009

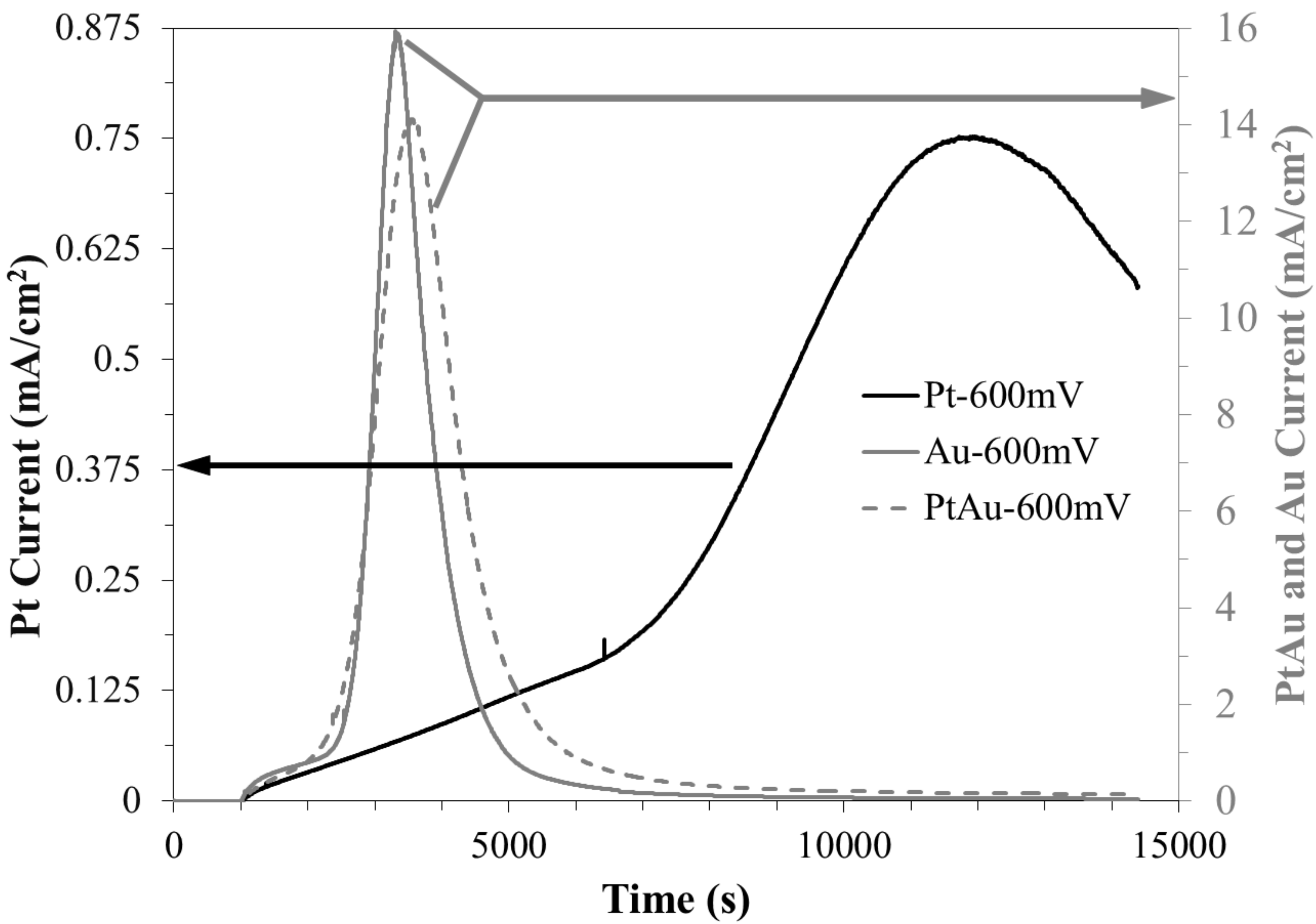
*SO2-Depolarized Electrolyzer

Accomplishments – Task 1 – Catalyst Testing Summary

- Catalysts have been identified that exceed current Pt performance
- Au and PtAu alloy catalysts meet the performance criteria
- PtV is a potential lower cost candidate showing promising results



Technical Backup Slides

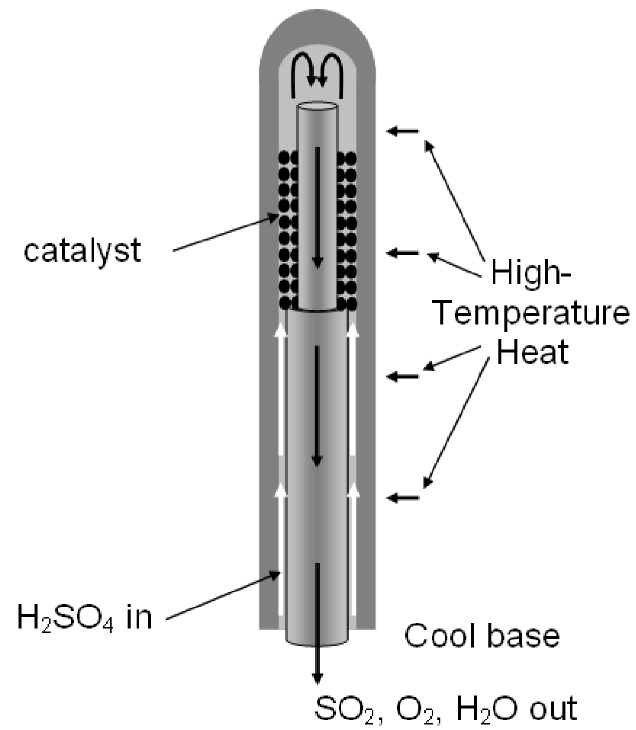


SDE Longevity Test Results

- **$600,000 "Funds-In" CRADA with Air Products and Chemicals established in 2013**
- **Goal: Demonstrate long-term HyS electrolyzer operation without sulfur formation**
- **Results:**
  - ***Refurbished single-cell test facility***
  - ***Established long-term testing capability***
  - ***Continuous SDE test for 1200 hours (no cell maintenance)***
  - ***1000 hours of H_2 generation at 10 lph H_2***
  - ***Post-test exam showed no sulfur formation***

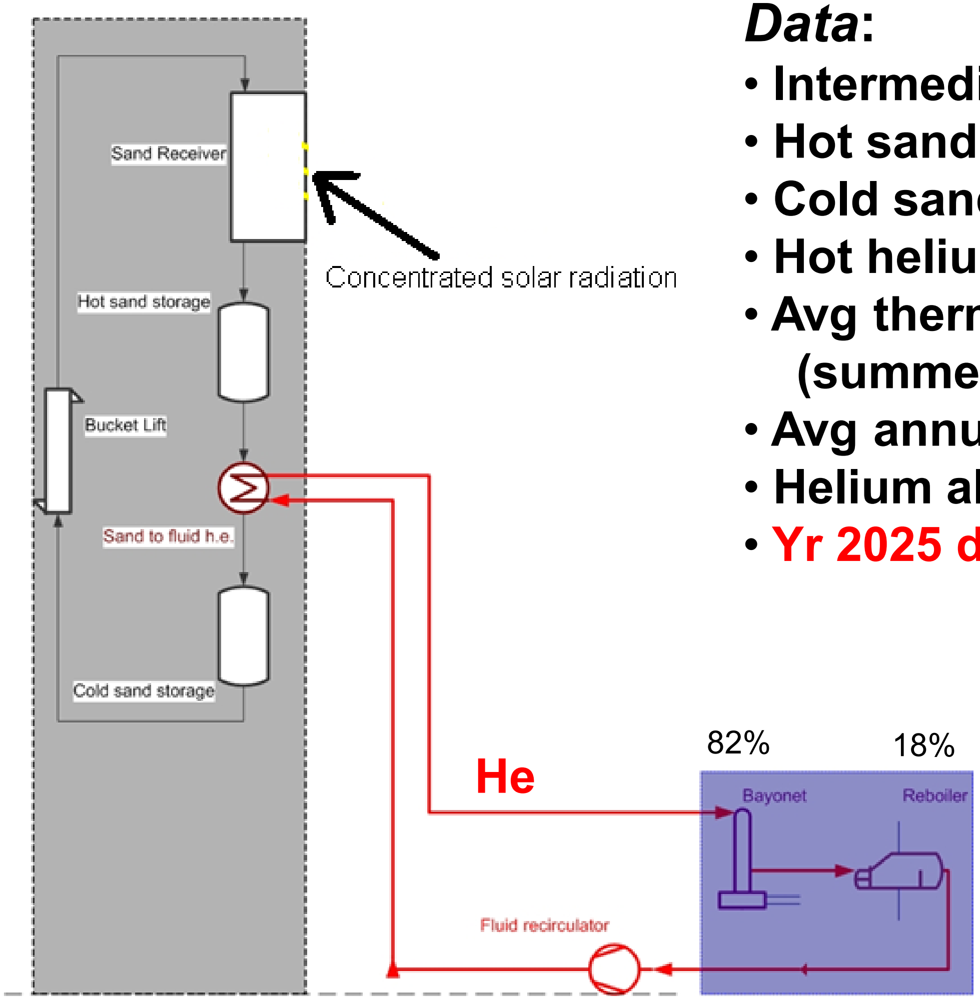
Step 2: Acid Vaporization and Decomposition

- 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

HyS Process Integration with Falling Particle Receiver



Data:

- **Intermediate fluid** **He**
- **Hot sand storage** **~1000 ºC**
- **Cold sand storage** **~600 ºC**
- **Hot helium** **950 ºC**
- **Avg thermal power (summer solstice)** **329 MW**
- **Avg annual H2 prod.** **100 TPD**
- **Helium also provides reboiler heat**
- **Yr 2025 design eliminates He loop**

Solar HyS Energy Input and Losses