
Electrolyzer Component Development for the HyS Thermochemical Cycle

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Project PD096

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Overview

Timeline

- Project Start Date: May, 2013
- Project End Date: September 30, 2014*

Budget

FY13 DOE Funding: \$300,000

Planned FY14 DOE funding:
\$75,000

Total DOE Project Value: \$375,000

Cost Share Percentage: 0

Total 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
- Partner: University of South Carolina
- 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.

Relevance – Project Objectives

Overall Objective

- Develop improved technology for the Hybrid Sulfur (HyS) thermochemical process to permit low-cost, highly efficient hydrogen production from concentrated solar energy
- Focus on the HyS SO₂-depolarized electrolyzer (SDE) using PEM technology

Fiscal Year 2014 Objectives

- Identify and quantify performance of anode electrocatalysts and advanced proton-exchange membranes to improve the efficiency and lower the capital and operating cost for the electrolysis step of the Hybrid Sulfur thermochemical process
- Address major challenges of faster reaction kinetics, high specific output (current density), elimination of sulfur formation, and longer operating lifetime for SDE
 - *Reduce anode kinetic overpotential by >100 mV*
 - *Identify and test high-temperature PEM membranes, including PBI, with high ionic conductivity, minimal or no sulfur dioxide transport, and physical integrity with potential to result in long-term goal of 500-600 mV cell potential at current densities of >500 mA/cm²*
- Demonstrate improved components thru button-cell operation at increased temperature (up to 130°C) and higher pressure (up to 10 atmospheres)

Relevance – Addressing Technical Barriers

Coupling Concentrated Solar Energy and Thermochemical Cycles

- Hybrid Sulfur Process is one of the most advanced thermochemical cycles
- SO₂-depolarized electrolyzer (SDE) is the key developmental component
- Improvements in SDE increase overall process efficiency and reduce cost-of-hydrogen

Materials and Catalyst Development

- Improvements in anode electrocatalysts lowers cell cost and improves efficiency (cell voltage)
- Higher temperature membranes can address several SDE issues, including improved cell voltage, higher current density, minimization of sulfur crossover, and longer cell lifetime

Chemical Reactor Development and Capital Costs

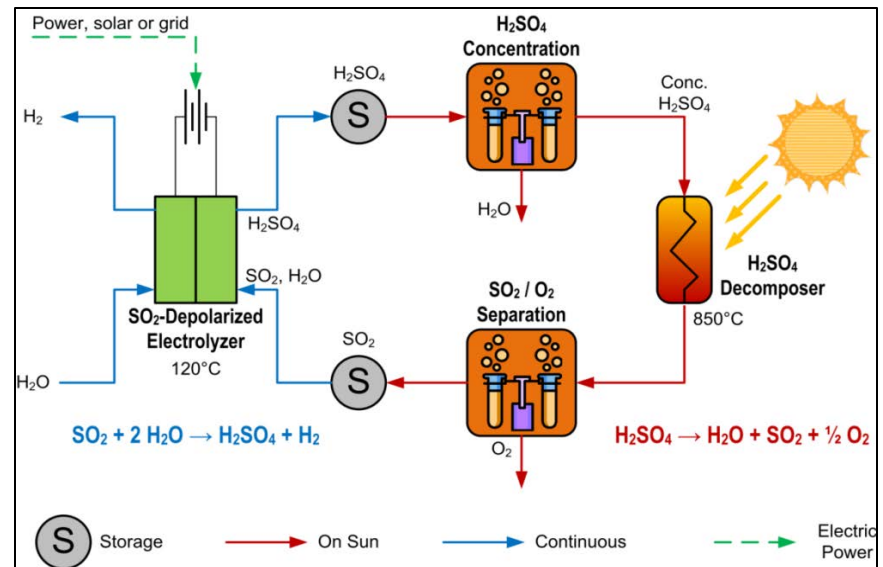
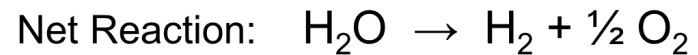
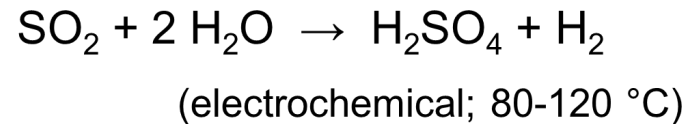
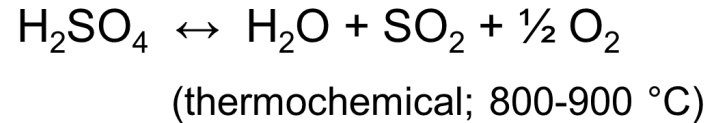
- SDE development, along with development of the balance of the solar HyS process, will enable meeting DOE hydrogen production goals of <\$3.70/kg and Solar-to-H₂ conversion >20%



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 SO₂ 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 cm² was performed for up to 200 hours at 80°C and 6 atm
- Higher temperature operation and improved catalysts & membranes were identified as future improvements

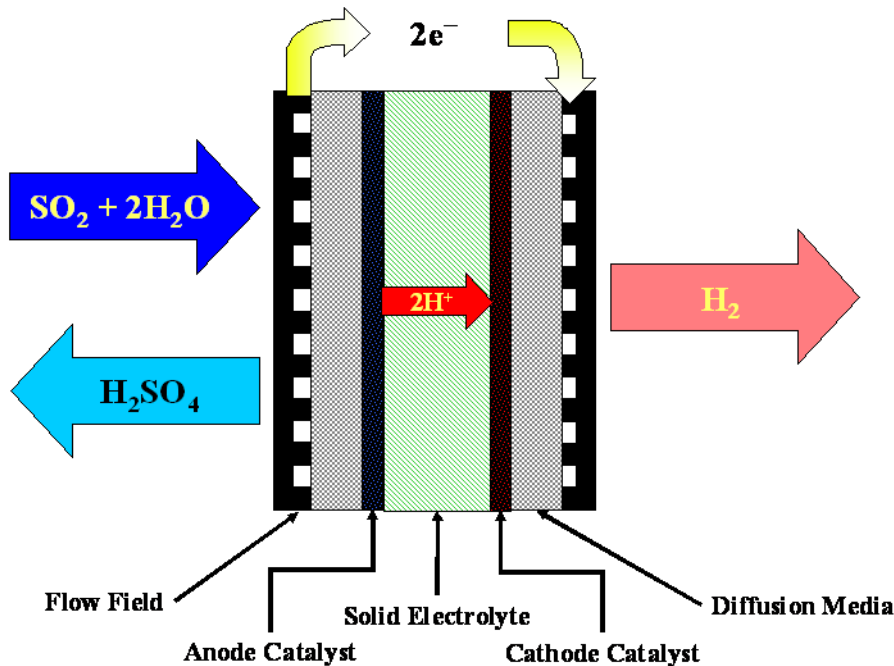
Hybrid Sulfur Chemistry



Solar HyS Process Schematic

Approach – SO₂-Depolarized Electrolyzer (SDE) Concept

SO₂-Depolarized Electrolyzer based on Proton Exchange Membrane (PEM) Design



- SO₂ is oxidized at the anode to form H₂SO₄ 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 SO₂ 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/cm² by 2020 to achieve MYRDD H₂ cost target of <\$3.70 per kg. Longer-term goal is 500 mV.



Approach – Technical Efforts Focus on Three Main Tasks

Task 1. Perform Anode Catalyst Screening in Model Solutions

- Losses due to oxidation kinetics at anode represent 70% of total SDE overpotential
- Perform rapid screening of electrocatalysts by sputter depositing on corrosion resistant coupons
- Evaluate Pt, Au, Ag and alloy catalysts in sulfuric acid saturated with SO₂

Task 2. Complete Fabrication of Pressurized Button Cell Test Facility

- Test facility design and partial assembly initiated previously under DOE-NE program
- Goal is to permit button-cell testing under HyS conditions of higher temperature & pressure
- Requires saturating sulfuric acid with SO₂ and recirculating acid solution (highly corrosive)

Task 3. Establish MEA Performance Baseline at SDE Conditions

- Fabricate membrane electrode assemblies (MEA) using advanced PEMs and catalysts
- Test MEAs for effects of different catalyst loadings, pressures and acid concentration at 90°C and 10 atmospheres; extend to 130°C as funding permits
- Collaborate with University of South Carolina on development of polybenzimidazole (PBI) membrane

Approach - Milestones

Task 1. Perform anode catalyst screening in model solutions

- Milestone 1.1: Complete anode catalyst screening for sulfur dioxide oxidation overpotential in conditions from 30 to 50 wt% H₂SO₄ for 3 or more different metal or alloy catalysts with the goal of identifying improved electrocatalysts with the potential to reduce the oxidation overpotential by >20 mV versus the current Pt catalyst. Due: 8/30/13 Status: Complete

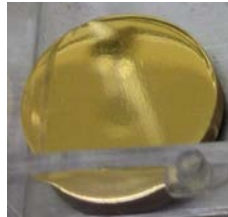
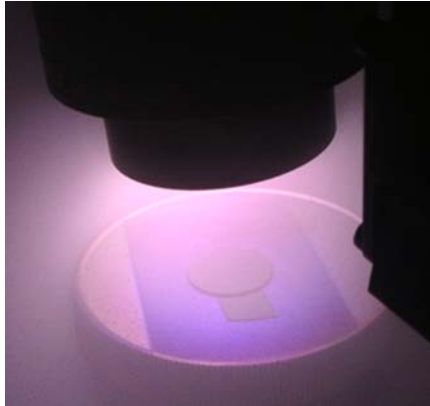
Task 2. Complete fabrication of Pressurized Button Cell Test Facility

- Milestone 2.1: Complete design and fabrication of major processing components for the PBCTF capable of operation at 130°C and 10 atm. Due: 12/31/2013 Status: Complete.
- Milestone 2.2: Complete fabrication and integration of all components into the PBCTF and initiate check-out testing at cell temperatures from 20°C to 90°C. Due: 3/31/14
Status: In Progress as of 4/15/14

Task 3. Establish MEA Performance Baseline at SDE Conditions

- Milestone 3.1: Complete Baseline Testing of Nafion® MEA at 60°C, 75°C and 90°C and at 2.5, 5 and 10 atmospheres. Due: 6/30/14 Status: On Schedule
- Milestone 3.2: Complete Performance Testing of Advanced MEAs (including a least one PBI membrane) at 90-130°C and 10 atmospheres. Due: 9/30/14 Status: On Schedule

Accomplishments – Task 1 – Catalyst Screening in Model Solutions



- **Rapid Screening**
 - Physical vapor deposition
 - Pt/Au-other metal alloys
- Experiment done in 30 wt% H₂SO₄ saturated with SO₂
- **Goal: Reduce overpotential by >20 mV vs Pt catalysts**



Accomplishments – Task 1 – Baseline Platinum Catalyst

$E_{\text{reversible}} = 173 \text{ mV}$

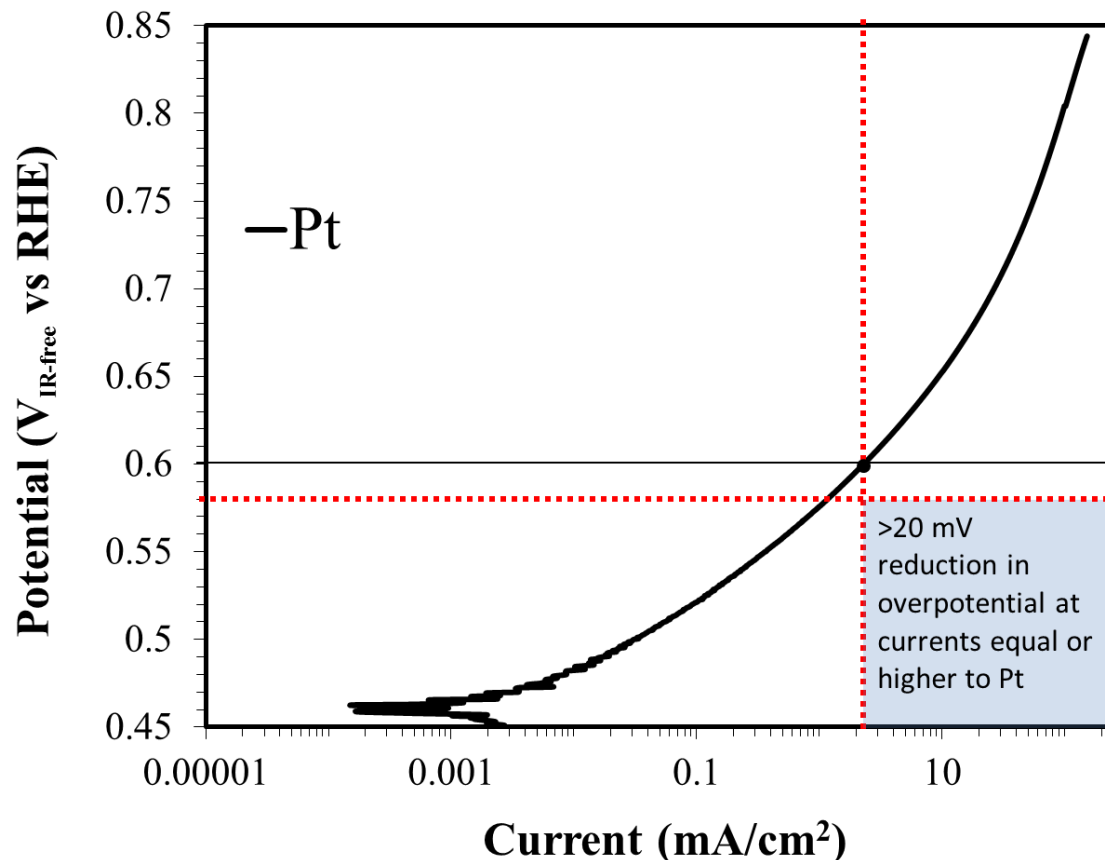
@ 20°C, 30 wt% acid

Test conditions

T= 22 °C

30 wt% H₂SO₄

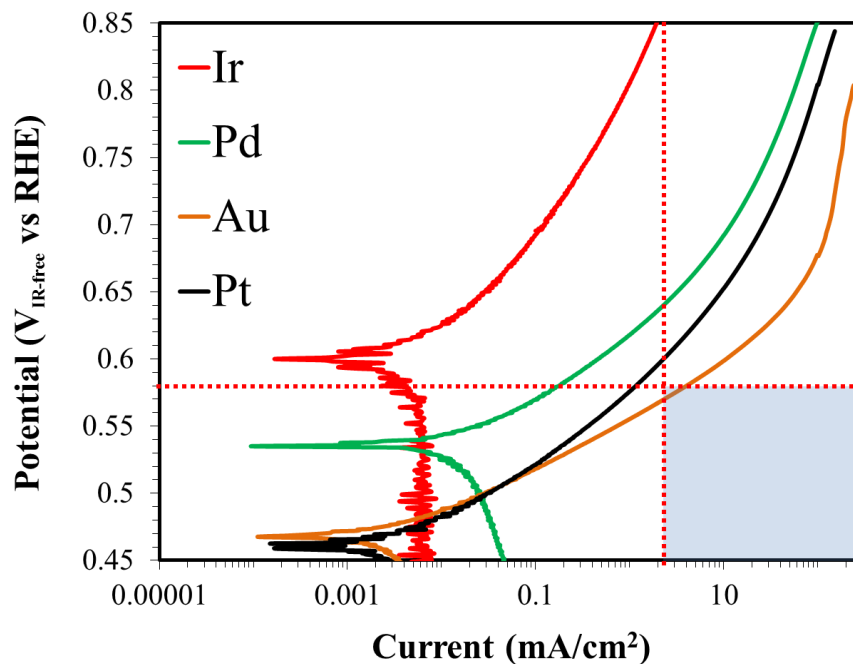
Saturated with SO₂



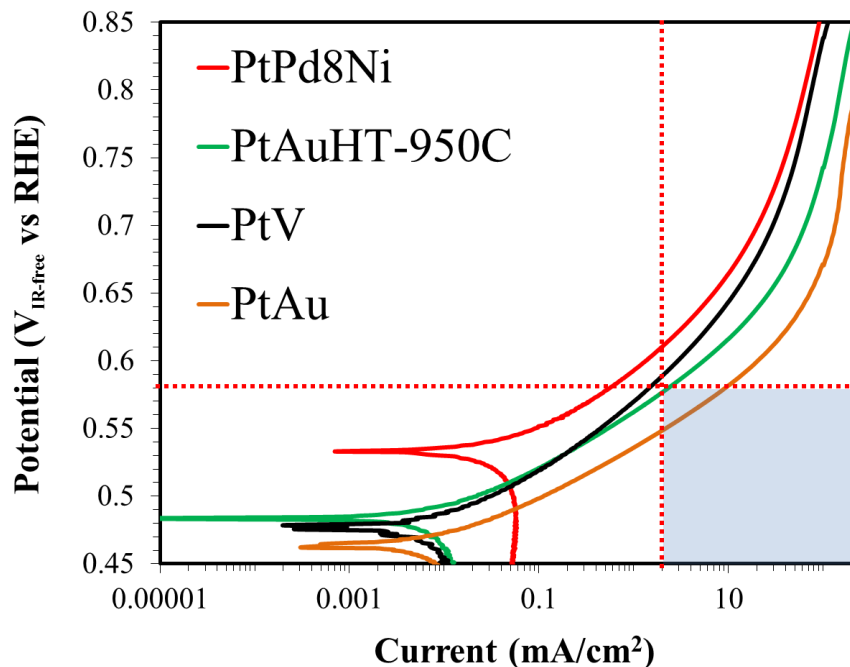
- Any catalyst that its performance curve falls inside the shaded area will meet the goal of reducing the overpotential by >20 mV vs Pt catalysts



Accomplishments – Task 1 – Catalyst Screening Results



Single metal catalyst testing:
Only Au meets performance target of <20 mV below Pt catalyst



Bimetallic catalyst testing:
Pt-Au and PtV meet the performance target



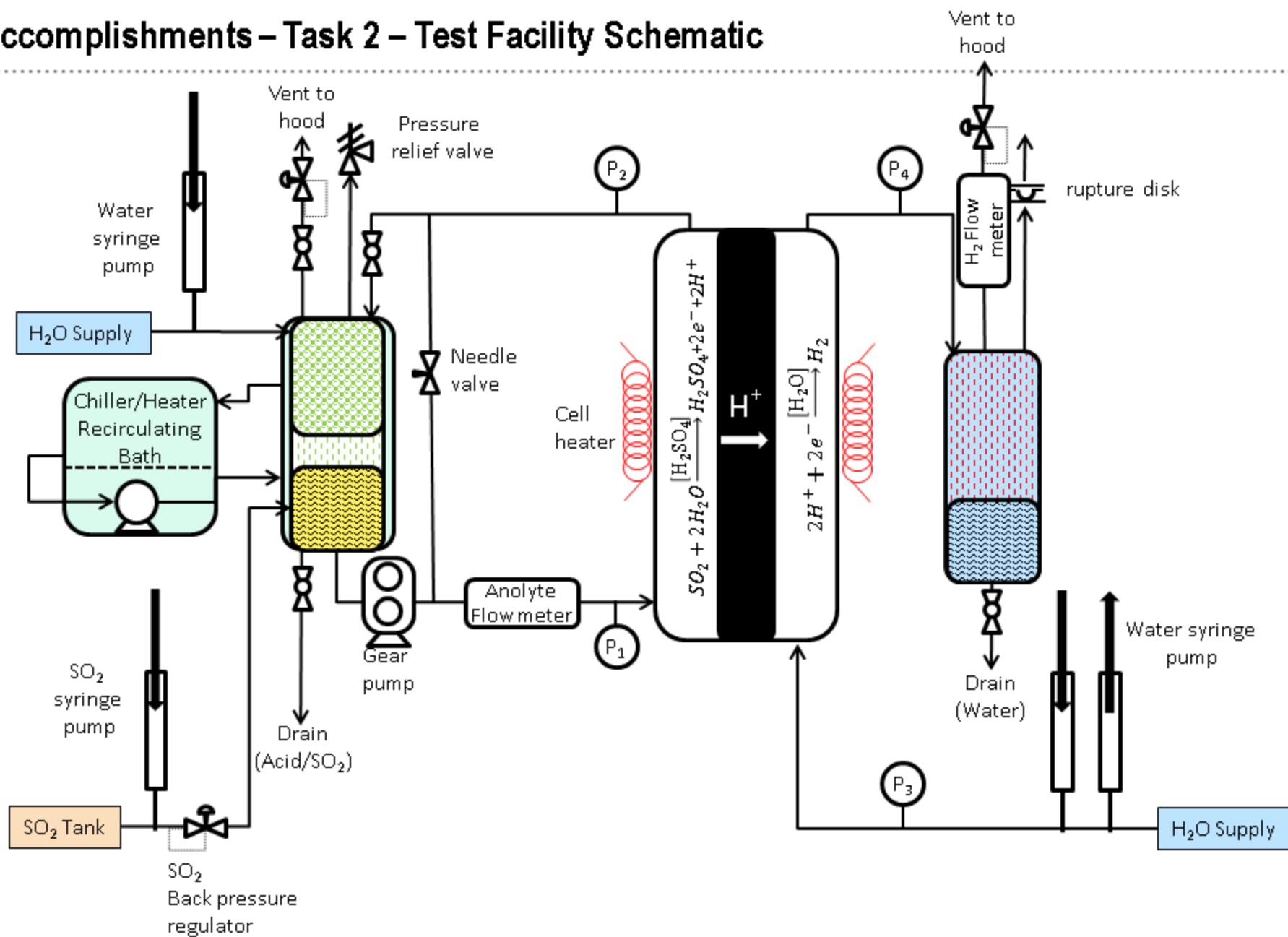
Accomplishments – Task 2 – Complete Fabrication of Test Facility

Pressurized Button Cell Test Facility (PBCTF)

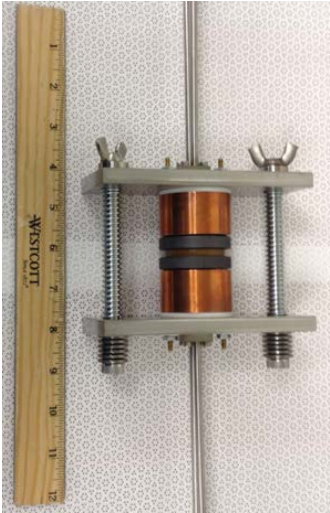
- Allows testing of electrolyzer components (membranes, catalysts, flow distributors) at high temperatures and pressures
 - *Prior button cell testing limits: 80°C and atmospheric pressure*
 - *Target higher performance: 130°C and 10 atmospheres*
- Requires more complex system to recirculate highly corrosive 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*



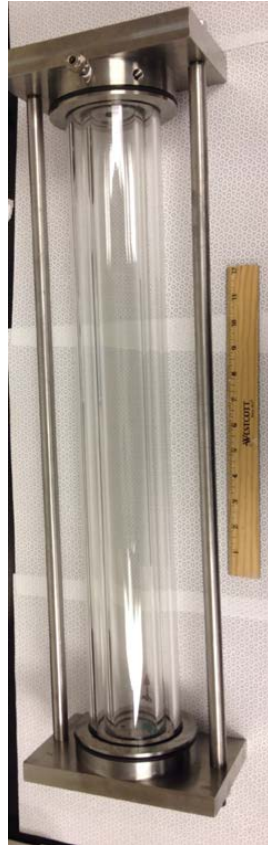
Accomplishments – Task 2 – Test Facility Schematic



Accomplishments – Task 2 – Completion of PBCTF



Electrolyzer Cell



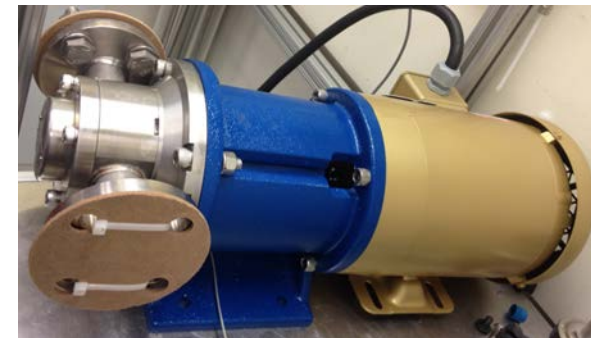
Zirconium Anolyte Tank

Hydrogen Separator Tank



PBCTF Status (4-15-2013)

- **Fabrication**
 - 90 % complete
- **Component Integration**
 - 60 % complete



Anolyte pump

Accomplishments – Task 3 – Performance Testing of Advanced MEAs

- **Goals and significance**

- Higher temperature is expected to improve anode kinetics and lower overpotential
- Improved electrocatalysts will further reduce kinetic overpotential
- Advanced PEMs can improve ionic conductivity and allow higher current densities
- Advanced PEMs can further reduce SO₂ crossover and eliminate sulfur formation
- Advanced PEMs, such as s-PBI, can operate with stronger acid concentrations
 - *More concentrated acid leaving the SDE reduces downstream energy requirements for acid concentration and subsequent decomposition in Step 2 of HyS process*

- **Test Plan**

- Prepare membrane electrode assemblies (MEAs) with catalyst/PEM combinations
- Establish performance baseline with Nafion® MEA at 60°C, 75°C and 90°C and at 2.5, 5 and 10 atmospheres
- Establish performance baseline with advanced MEAs (including s-PBI) at 90°C
- Test effects of electrocatalyst loading, T&P and acid concentrations

- **Testing will begin immediately following completion of Task 2**

Accomplishments – Responses to Previous Year Reviewers' Comments

- **Project was not reviewed last year**
- **Project began May, 2013**
 - Poster presentation was given at 2013 AMR, but not reviewed



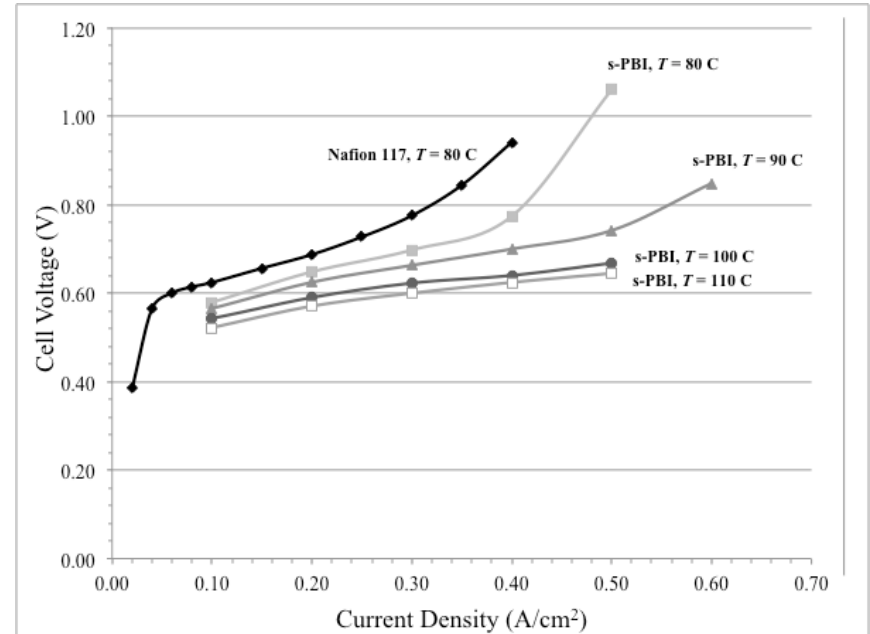
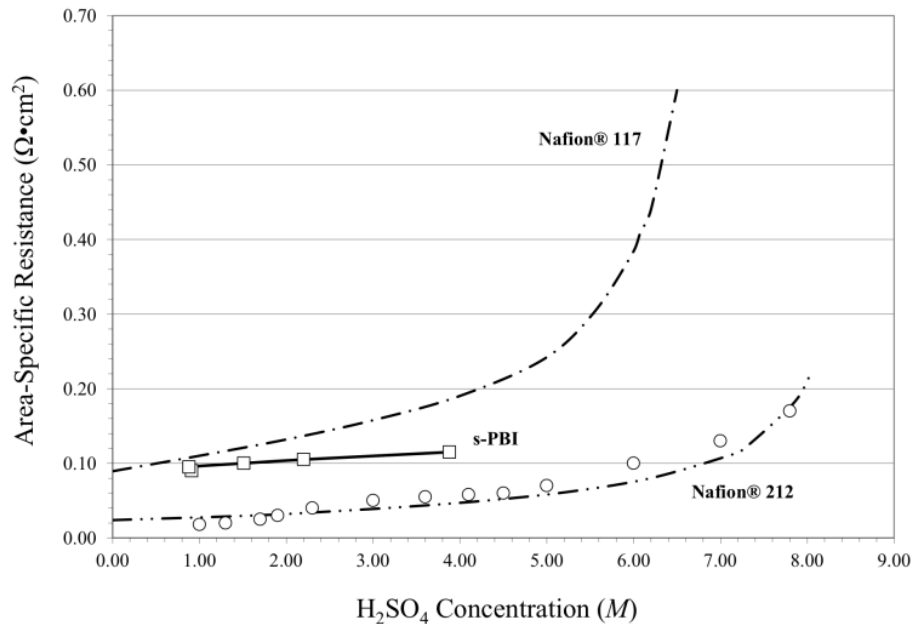
Collaborations – University of South Carolina

- SRNL collaborated with Dr. John Weidner and his team at USC for SDE development during the prior DOE-supported HyS program (2005 – 2010)
- USC focused on testing of gaseous-fed button cell, modeling of SDE operation and development of new membranes
- USC has continued an internally-supported program to develop their sulfuric acid doped PBI membranes (s-PBI)
 - *Initial results showed superior results as compared to Nafion®*
 - *Initial results showed low concentration acid production on gaseous-fed SDE*
 - *Recent data showed improved acid production (~12M)*
 - Need performance improvement, but data is stable and promising
 - *Data shows that with increased P and T , the performance can be improved while producing highly concentrated acid (s-PBI capable of $>140^{\circ}\text{C}$ operating temperature)*
 - Nafion® performance degrades at an accelerated rate at concentrations ≥ 40 wt% acid
- 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
- Results will be compared to USC's gaseous-fed SDE test results



Collaborations – Membrane Development at University of South Carolina

- Comparison of Nafion® and PBI membranes
- Water added to cathode for Nafion® and added to 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 or liquid-fed anolyte (SO₂-saturated sulfuric acid)



Remaining Challenges and Barriers

- **Increasing the temperature and pressure of the PBCTF requires design and fabrication of specialty components for test facility**
 - Corrosion resistant small-size parts (e.g. anolyte pump) are not available commercially
- **s-PBI membranes require water to be introduced on anode-side of cell**
 - Need to develop alternative anode humidification process at USC for gas-fed cell
 - Need to measure performance using liquid-fed anolyte
- **Continued improvement in performance**
 - Demonstrate high current density operation ($>500 \text{ mA/cm}^2$) at high T&P
 - Further reduce cell voltage (600 mV by 2020; long-term goal of $<500 \text{ mV}$)
 - Determine voltage degradation rates for long-lifetime operation ($>40,000 \text{ hrs}$)
- **Verification of sulfur-free operation using advanced MEAs**
- **Commercial SDE design needs to be cost-effective**
 - Scale-up cell area and continue design efforts for large capacity commercial electrolyzer (1 m^2 active cell area)

Future Work

- **Improvements in SDE performance using higher T&P and advanced catalysts and MEAs need to be demonstrated**
- **Planned FY14 Work:**
 - Complete test facility and initiate testing of MEAs with PBCTF (Milestone 2.1)
 - Complete Baseline Testing (Milestone 3.1)
 - Collaborate with University of South Carolina on s-PBI development
 - Complete Performance Testing of Advanced MEAs (Milestone 3.2)
- **FY15 and Future Work**
 - Additional work contingent upon approval and direction by DOE
 - Continue R&D to improve cell performance
 - Conduct long-term tests of advanced membranes; determine degradation rates
 - Conduct single cell testing (60 cm² active cell area) of advanced MEA at high T&P
 - Scale-up and perform closed-loop integrated lab-scale demonstration of Hybrid Sulfur Process combining SDE with acid decomposition reactor

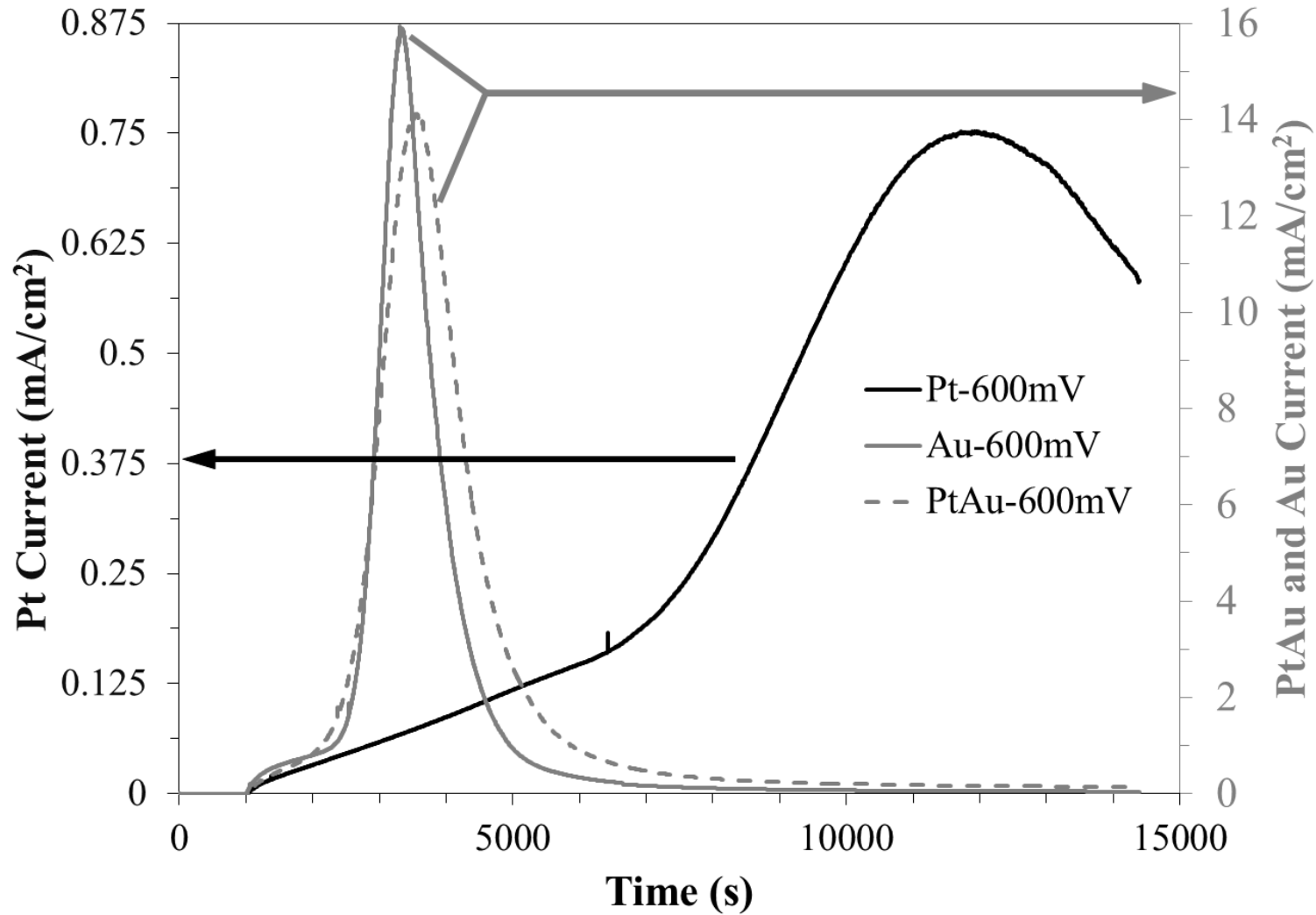
Project Summary

- **Relevance** The SO₂-depolarized electrolyzer (SDE) is the key component for enabling cost-effective solar hydrogen production using the Hybrid Sulfur process
- **Approach** Develop electrocatalysts and advanced proton-exchange-membranes for the SDE operating at higher temperature and pressure to permit lower cell voltage (higher electrolysis efficiency) and produce more concentrated acid product (higher overall system efficiency)
- **Technical Accomplishments** 1) Identification of improved electrocatalysts using Pt and Au alloys; 2) Design and construction of a high temperature/pressure button cell test facility to permit accelerated testing; 3) Collaboration with University of South Carolina to develop sulfonated polybenzimidazole (s-PBI) membranes with superior performance
- **Future Work** Fabricate MEAs using new catalysts and membranes and complete performance testing in FY14. Dependent on funding, continue SDE development, including endurance testing, larger single cell testing, and integration of SDE with balance of Hybrid Sulfur process

Technical Back-Up Slides

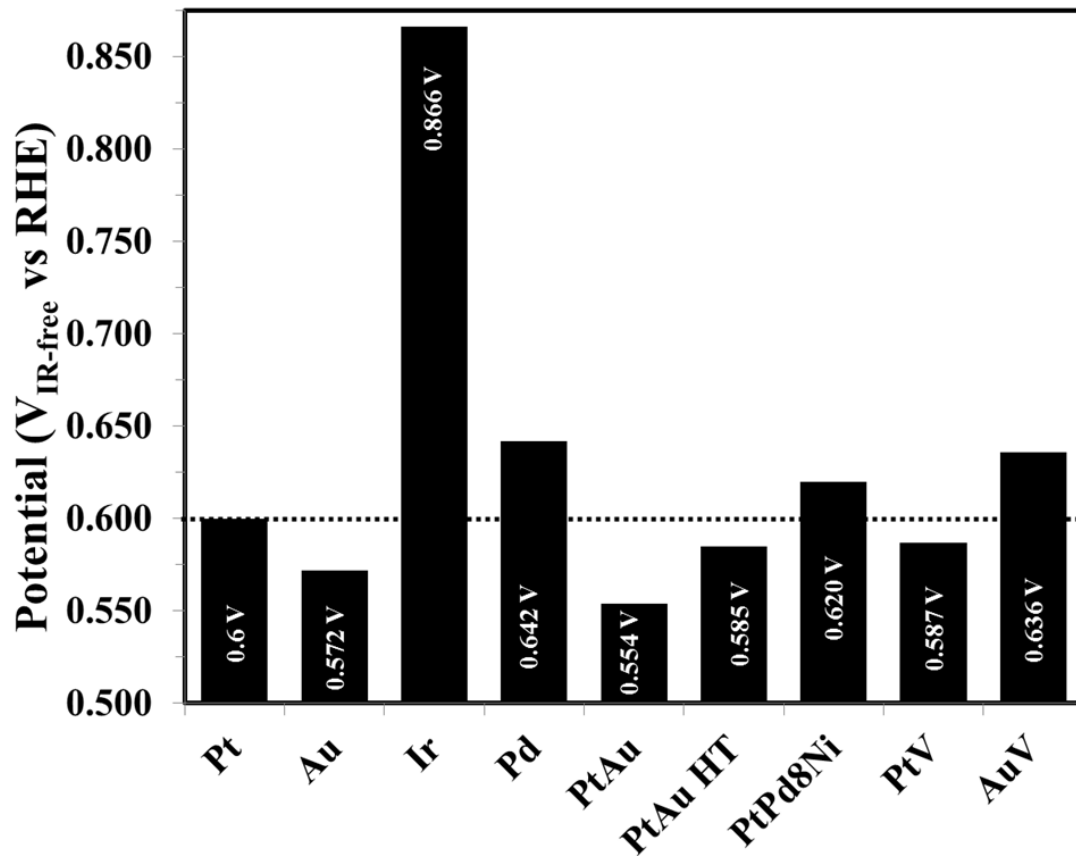


Technical Backup Slides

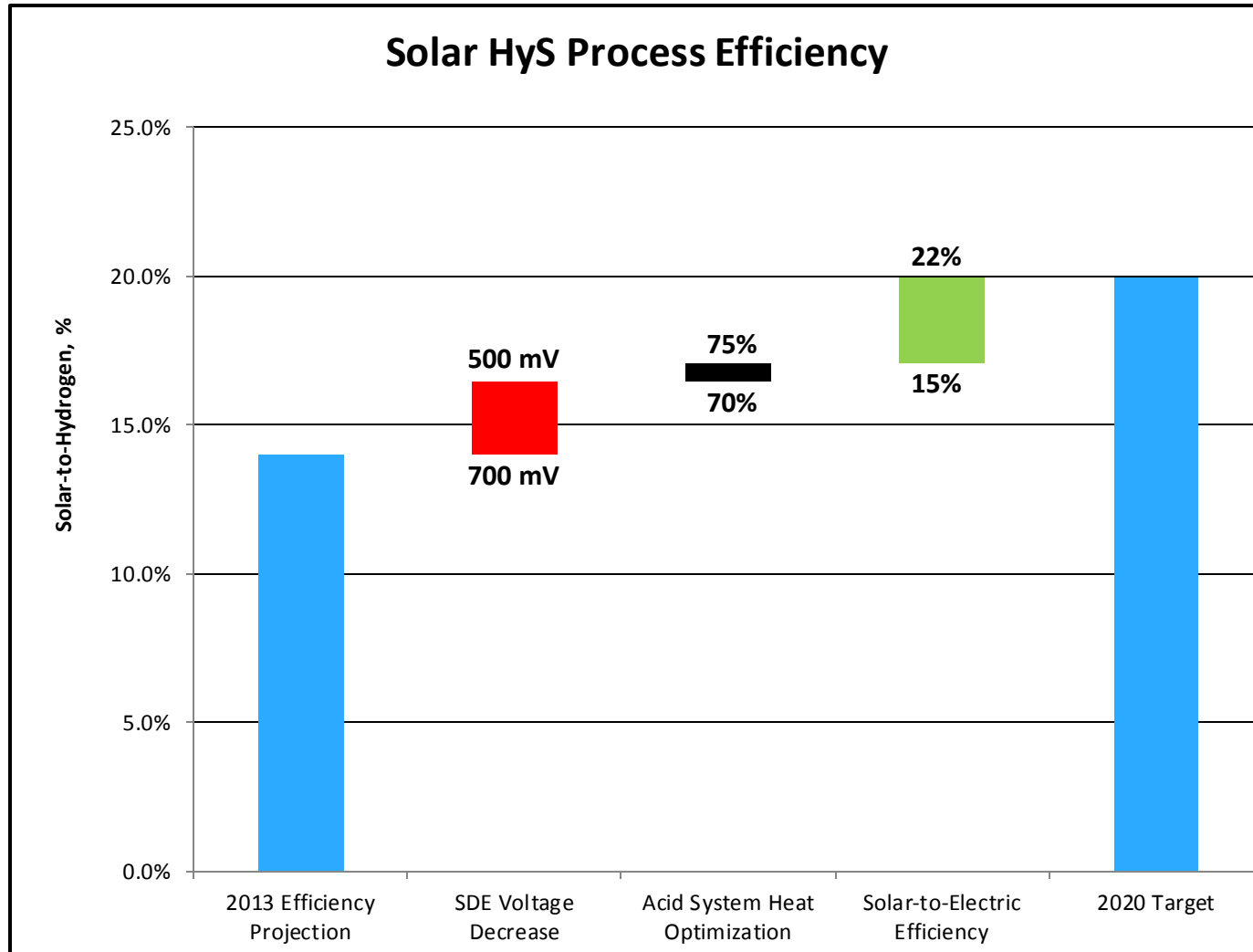


Accomplishments – Task 1 – Catalyst Testing Summary

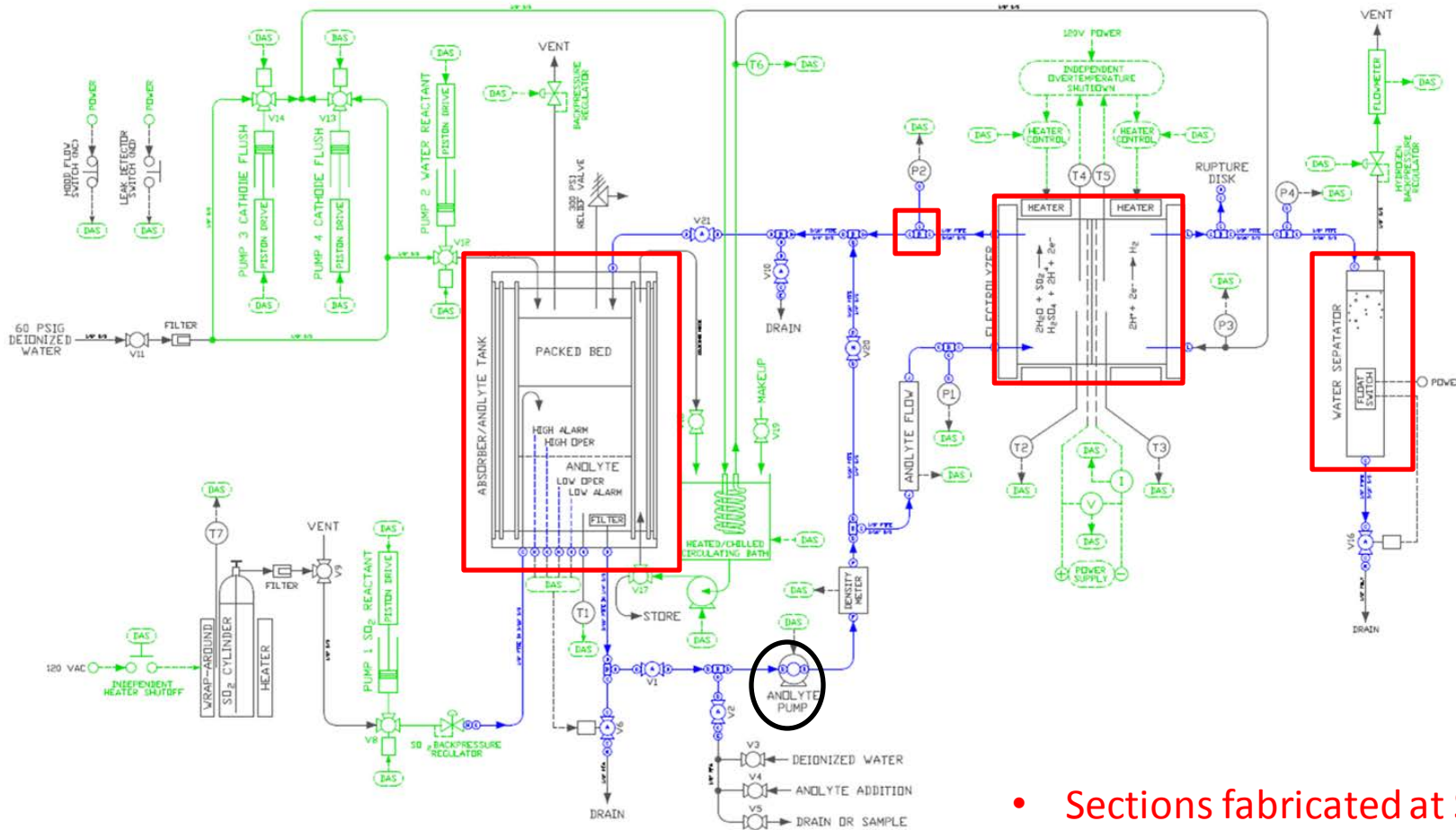
- Catalysts have been identified that exceed current Pt performance
- Au and PtAu alloy catalysts meet the performance criteria
- PtV is a potential lower cost candidate showing promising results



Technical Backup Slides



Technical Back-up Slides



- Sections fabricated at SRNL
- Anolyte Pump