Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

WHEC 2014
20th World Hydrogen Energy Conference 2014
June 15[Sun] ~ 20[Fri], 2014 KDJ Convention Center, Gwangju Metropolitan City, Korea

Direct solar hybrid sulfur water-splitting process for continuous centralized hydrogen production

Lloyd C. Brown[b], Chau-Chyun Chen[e], Héctor R. Colón-Mercado[a], Daniel M. Ginosar[d], Maximilian B. Gorensek[a,*], John R. Monnier[d], Martin Roeb[c], William A. Summers[a], Dennis Thomey[c], John W. Weidner[f], Bunsen Wong[b]

[a] Savannah River National Laboratory, Aiken, SC 29808 USA
[b] General Atomics, 3550 General Atomics Ct., San Diego, CA 92121 USA
[c] German Aerospace Institute (DLR), Institute of Solar Research , Koeln, 51147 Germany
[d] Idaho National Laboratory, PO Box 1625, Idaho Falls, ID 83415 USA
[e] Texas Tech University, Department of Chemical Engineering,
[f] University of South Carolina, Department of Chemical Engineering

ABSTRACT

An international team is planning to develop a virtual demonstration of solar thermochemical hydrogen production based on the hybrid sulfur cycle. The effort will couple DLR's diurnal two-chamber solar reactor with SRNL's continuous PEM SO_2-depolarized electrolyzer. General Atomics will help integrate the two halves of the process and will contribute the SO_2 separation and H_2SO_4 handling components. Other partners include INL, Texas Tech University, and the University of South Carolina, who will work on improved catalysts for both reaction steps, improved PEM membranes for electrolysis, and a properties model that accurately duplicates the highly non-ideal behavior of the SO_2-H_2SO_4-H_2O-SO_3-O_2 system. The solar acid decomposition system will be tested on-sun at DLR's solar furnace/simulator in Cologne, Germany, the electrolyzer will be tested at SRNL, and the acid/SO_2 system will be tested at GA. Virtual integrated operation will be achieved by matching interface conditions between systems and utilizing process simulation models. While the scale of the demonstration is small ($\geq$3 L H_2), the project objective includes a detailed commercial scale design together with economic analyses to generate credible estimates for the cost of hydrogen production.

Keywords: Hybrid Sulfur (HyS) Cycle, Solar, Demonstration, Integrated Operation, Economic Analysis

1. Introduction

1.1 Background

The well-known hybrid sulfur (HyS) cycle [1] is the only practical, all fluid, two-step thermochemical cycle. A concentrated solar receiver can serve as the high temperature heat source, in which case the first step uses solar energy to vaporize and decompose sulfuric acid (H_2SO_4), splitting it into water, oxygen (O_2), and sulfur dioxide (SO_2). The resulting SO_2 is combined with water and electrochemically oxidized in the second step, which utilizes an SO_2-depolarized electrolyzer (SDE) to make H_2SO_4 at the anode and hydrogen (H_2) at the cathode. All sulfur species are recycled and the overall reaction is the splitting of water to form H_2 and O_2. Excess SO_2 is stored during daylight operation and used at night to permit continuous electrolyzer operation and H_2 production. Electricity is supplied from a companion solar-electric plant or obtained from the grid. Approximately 80% of the energy input to the process is solar thermal energy; only 20% is electricity for the electrolyzer and auxiliaries.

* Corresponding author. Tel.: +1-803-725-1314, Fax: +1-803-725-0141, E-mail: maximilian.gorensek@srnl.doe.gov

Westinghouse Electric Corporation began work on the HyS cycle in the early 1970s as a way to use high temperature heat from advanced nuclear reactors to split water and produce H_2. They succeeded in demonstrating a lab-scale closed-loop version of the process constructed of glassware and heated electrically. Development also took place in Europe at the Joint Research Center in Ispra, Italy and at the Nuclear Research Center (KFA) in Jülich, Germany. As a result of the significant decline in worldwide research on advanced nuclear technologies beginning in the early 1980s, most thermochemical H_2 development activities ceased for nearly 20 years. Beginning in 2001, an increased U.S. national interest in both H_2 energy and advanced nuclear reactors resulted in the U.S. Department of Energy (DOE) supporting new research for both nuclear- and solar-based thermochemical H_2 production. Savannah River National Laboratory (SRNL) led a major research program for the DOE Office of Nuclear Energy (NE) from 2003-2009 under the Nuclear Hydrogen Initiative (NHI). In a collaborative program, the University of South Carolina (USC) developed detailed models of electrolyzer performance and identified promising new membranes that demonstrated significant cell performance improvements. As part of the DOE Solar Thermochemical Hydrogen program (STCH), SRNL adapted the plant design for integration with a concentrated solar power system. Independent assessment based on the DOE H2A analysis tool showed HyS to have the second lowest cost of H_2 among all thermochemical cycles studied [2]. In fiscal year (FY) 2013, SRNL initiated new research funded by DOE aimed at developing improved catalysts and electrolyzer membranes for the SDE. Also in 2013, SRNL successfully conducted a 1,000-h continuous test of the laboratory-scale electrolyzer under a cooperative research and development agreement with an industrial partner.

Work on the high temperature acid decomposition step in the U.S. was conducted under NHI by Sandia National Laboratory and General Atomics (GA). They demonstrated operation of a lab-scale H_2SO_4 decomposition system for integration with the sulfur iodine thermochemical cycle, which has the same high temperature step as the HyS cycle. Their primary challenges were the materials of construction and the decomposition catalyst. Under a European Union (EU) program, the German Aerospace Center (DLR) has focused on developing solar systems and components for the catalytic decomposition of H_2SO_4, and they have successfully demonstrated a direct solar-heated laboratory-scale acid vaporizer and decomposition system.

1.2 Objective

As a result of these extensive research efforts, HyS is one of the most advanced of the thermochemical H_2 cycles. However, major technical barriers and shortcomings remain to be overcome. Led by SRNL, a team that includes DLR, GA, Idaho National Laboratory (INL), Texas Tech, and USC has been formed to develop a solar HyS process. The goal of this team is to demonstrate HyS technology with a concentrated solar heat source. Targeted improvements include: (1) demonstrating catalysts and membranes that will reduce the electrolyzer operating voltage to <500 mV with long-term stable performance; (2) demonstrating robust materials for the acid vaporizer and catalysts with acceptable lifetimes that will achieve acid decomposition at near equilibrium conversion at $\leq 850^\circ$ C, and (3) demonstrating bench-scale SO_2 separation that validates the flowsheet design and the project economics. The project will culminate in a virtual system demonstration of >8 h of continuous operation in sunlight with a cumulative production of at least 3 standard L of H_2. Based on these success factors and a rigorous modeling and simulation program, a revised plant performance and H2A cost analysis will be performed to demonstrate the capability of achieving the DOE 2020 Multi-year Research, Development and Demonstration (MYRDD) goals of a solar-to- H_2 energy conversion ratio of $\geq 20\%$ and a cost of H_2 of $\leq \$3.70$/kg.

2. Technical Overview

The HyS cycle comprises two coupled reaction steps. The thermochemical step, which is common to all thermochemical sulfur cycles, is the high-temperature decomposition of H_2SO_4 into water, SO_2, and O_2.

$$H_2SO_4(aq) \xrightarrow{\text{Heat, T>800°C}} H_2O(g) + SO_2(g) + \frac{1}{2}O_2(g)$$

This is an equilibrium-limited reaction that requires a catalyst, as well as heat input at relatively high temperatures, such as those obtainable with a high temperature nuclear reactor or a concentrated solar receiver. The electrochemical step is the SO_2-depolarized electrolysis of water, which takes place at lower temperatures and consumes electric power.

$$SO_2(aq) + 2H_2O(l) \xrightarrow{\text{Power, T}\approx 80-120°\text{C}} H_2SO_4(aq)$$

The combined net effect of the two reactions is the splitting of one mole of water into one mole of H_2 and one-half mole of O_2. The major advantage of SO_2-

2014 WORLD HYDROGEN ENERGY CONFERENCE 2014 whec2014.com

depolarized electrolysis is a substantial reduction in the electric power requirement compared to conventional direct water electrolysis (-0.158 V standard potential at 25°C versus -1.229 V for water electrolysis, a reduction of 87% in theoretical work). Irreversibilities caused by kinetic and mass transfer limitations and Ohmic losses, as well as economic considerations, lead to water electrolyzers typically being operated at 1.8 to 2.0 V. In contrast, SDEs are expected to be capable of achieving 0.5 to 0.6 V at practical current densities, thus requiring less than one-third as much electricity per unit of H_2 produced as conventional water electrolysis.

Figure 1 presents a simple system schematic of a Solar HyS H_2 production process. Each of the major processing areas of the plant is discussed in the following sections.

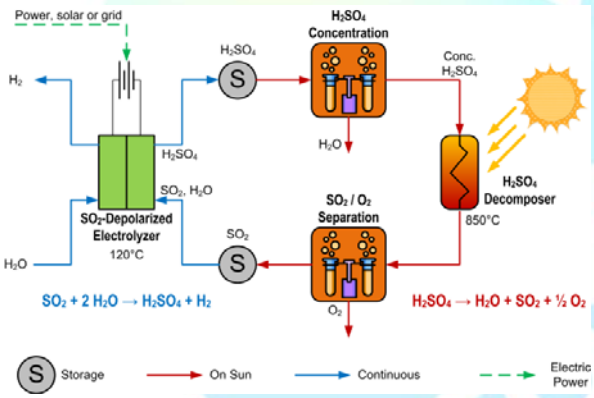

Figure 1. Solar HyS H_2 Production Process

2.1 SO_2-Depolarized Electrolyzer

The original SDE developed by Westinghouse consisted of a conventional two-compartment parallel plate electrolyzer. A major improvement introduced by SRNL was the use of a proton exchange membrane (PEM) design modeled after work being performed for PEM fuel cells. The cell was operated using liquid anode feed in the form of SO_2 dissolved in sulfuric acid. Water was introduced into the cathode side to maintain membrane hydration. SRNL conducted multiple runs of over 200 h in a lab-scale electrolyzer (10 lph H_2 output) and demonstrated pressurized operation, small stack operation, and operation without sulfur accumulation, a major technical challenge [3]. Typical performance was a cell voltage of 760 mV at the desired current density of 500 mA/cm^2, which was achieved at 80°C using a Nafion® membrane. Proposed improvements aimed at reducing the voltage to 500-600 mV include increased operating temperature, advanced membranes, and higher activity electrocatalysts. The heart of the electrolyzer is the membrane electrode assembly (MEA), which consists of a PEM with catalyst coated on each side to create an anode and a cathode. The challenges for the membrane include the capability to maintain high proton conductivity at high acid concentrations, low gas permeability, and high thermal stability. For the catalysts, the challenges include materials with high activity that exhibit long-term stable performance under the SDE operating conditions. Specifically, anode catalysts must provide rapid SO_2 oxidation reaction kinetics, whereas the cathode catalysts must provide rapid reaction kinetics for H_2 formation in the presence of sulfur containing species, while avoiding the formation of elemental sulfur.

2.1.1 Catalyst Development – Most of the electrolysis inefficiencies arise from slow kinetics at the anode catalyst layer. For example, the reversible cell potential for the electrochemical oxidation reaction of SO_2 with 30 wt% H_2SO_4 saturated with SO_2 at room temperature is 172 mV. However, because of the kinetic inefficiencies, overpotentials of approximately 340 mV are observed at the anode during operation. Research on anode electrocatalysts has focused on the materials that decrease the overpotential and increase the material stability. Early work by Westinghouse showed palladium (Pd) to have the highest performance for the electrochemical oxidation of SO_2, followed by gold (Au) > platinum (Pt) > ruthenium (Ru). Later work performed at SRNL [4] compared the stability and activity of supported Pt and Pd nanoparticles on high surface area carbon black. The results showed that not only are Pt nanoparticles more active for the oxidation of SO_2, but Pt is also more stable than Pd. The discrepancy between SRNL results and those reported earlier was attributed to the use of nanoparticles vs bulk material. Recent work performed by O'Brien et al. [5] studied the anodic performance on Pt and Au electrodes. Their work not only showed Au being more active than Pt, but in addition Au did not require activation cycles as Pt does to reach optimum performance. Renewed research at SRNL revisited the study of Pt, Au, Pd, and iridium (Ir) as thin films. Preliminary results indicate that thin films made of Au, Pt-Au and Pt-vanadium (Pt-V) show higher activity than pure Pt electrodes and lower the overpotential to 290 mV (a 50 mV improvement). SRNL's results show that further anode development can result in lowering the overpotential and therefore increasing the efficiency of the SDE.

Although the kinetics of the Pt cathode electrode are much higher than those of the anode side, crossover of sulfur species through the membrane can have a deleterious effect on the reaction rate. Due to the susceptibility of Pt based electrocatalysts to sulfur species, the effect of sulfur contaminants on Pt-supported electrocatalysts has been specially covered in the literature for the PEM fuel cell electrodes. Results

THE WORLD HYDROGEN ENERGY CONFERENCE 2014
whec2014.com

specifically looking at the effects of SO_2 have shown a decrease in the H_2 desorption region of cyclic voltammograms, indicating the poisoning of the Pt sites at low potentials (<0.8 V), which in turn shows a decrease on the availability of free Pt sites for the adsorption of H_2. Improvements in cathode electrodes could result in potential gains close to 100 mV if the effects seen for the H_2 oxidation reaction in fuel cells are seen in the proton reduction reaction in the SDE.

2.1.2 Membrane Development – The PEM must be stable in a highly corrosive solution (>50 wt% H_2SO_4 saturated with SO_2) and at high operating temperature (>80 °C), minimize transport of SO_2 from the anode to the cathode, and must maintain high ionic conductivity. A result of SO_2 transport through the PEM is the undesirable production of hydrogen sulfide (H_2S), followed by the formation of elemental sulfur from the reaction of SO_2 with H_2S through the Claus reaction. Experiments at SRNL using Nafion® membrane have shown the effects of the SO_2 crossover to be the formation of a sulfur rich layer which causes mechanical damage to the MEA. An operating approach was developed to minimize damage from SO_2 crossover, but development of a PEM which limited SO_2 transport would be highly beneficial. Previous work at SRNL [6] studied the performance of a large number of membranes of different chemistry and designs to decrease the SO_2 crossover while maintaining high proton conductivity and membrane integrity. Membranes studied included hydrocarbon, fluorocarbon, and hydrocarbon/fluorocarbon blends. Among the membranes tested, polybenzimidazole (PBI) showed the best improvement over the Nafion® baseline. Recent work by USC [7] has focused on modifying the PBI membrane with H_2SO_4 as the doping solution in order to make it compatible with SDE operation. Results show the PBI membrane to have favorable performance (including low IR losses) compared to that of Nafion®. They also have the capability of operating at higher H_2SO_4 concentrations and at elevated temperatures (up to 120-140°C), which would help reduce kinetic losses and lower the cell voltage.

2.2 Solar Receiver and H_2SO_4 Decomposition

In order to provide high temperature heat to drive the decomposition of H_2SO_4 with solar energy, a conventional heliostat field and power tower is foreseen in this project. These components are well-known technologies currently being commercialized. The major development item is the solar receiver/reactor for conducting the acid decomposition. The operating conditions of high temperatures and particularly corrosive environments require advanced materials for the key components and therefore special design and fabrication methods. Several research groups have been studying reactor concepts for decomposition of H_2SO_4 by solar energy. GA developed and tested a cavity reactor constructed of steel tubes filled with catalyst [8]. The solar radiation is absorbed on the surface of the walls and transferred to the reactants via heat conduction. Hence, the maximum temperature of this concept is restricted by the upper temperature limit of the steel, about 900°C. Another concept making use of an inert energy carrier was proposed by Kolb et al. [9] as follows: sand is heated in a solid particle receiver on a solar tower and flows across a tubular heat exchanger heating the reactants inside of the tubes. As in the GA concept, the heat is transferred through the wall of the reactor, limiting the temperature of the process.

By contrast, the direct solar receiver/reactor concept proposed by DLR allows for higher temperatures (>1,000°C) and can, therefore, significantly increase the efficiency of the process. DLR has been developing a two-chamber direct solar receiver/reactor design as part of the European research projects HYTHEC [10] and HycycleS [11]. Chamber 1 vaporizes and thermally decomposes H_2SO_4 into sulfur trioxide (SO_3) and water in silicon carbide (SiC) foam under solar radiation. Chamber 2 uses solar radiation to catalytically decompose SO_3 into SO_2 and O_2 in a SiC honeycomb. A two-chamber reactor prototype at the 10-kW_{th} scale has been built, and successfully tested on sun in a solar furnace by DLR [12]. This experimental work was accompanied by modeling of the evaporator and the SO_3 decomposer. During these experiments and in long term corrosion tests, SiC turned out to be the material of choice for the solar absorbers facing the most corrosive environment. The direct solar evaporator concept needs to be redesigned and tested in a solar furnace/simulator before scale-up. Moreover, coatings for metallic materials of construction need to be developed, especially for the particularly corrosive boiling sulfuric acid evaporator environment.

Candidate catalysts for high temperature SO_3 reduction have been screened and analyzed, primarily considering transition metal oxides. A chromium-iron (Cr-Fe) mixed oxide was the most promising material among the ones examined [13], although further catalyst improvements, such as lower temperature operation capability, are desirable. The overall conversion of the H_2SO_4 cracker could be significantly increased if a suitable catalyst were introduced to operate in the lower temperature range closer to the outlet of the acid vaporizer (600°C). Whereas metal oxide based catalysts demonstrated high and stable activity for SO_3 decomposition at higher temperatures, they are

2014 WORLD HYDROGEN ENERGY CONFERENCE 2014 www.whec2014.com

deactivated at lower temperatures due to sulfate formation. Recently, copper vanadate based materials were developed for these conditions with promising conversion results [14]. Pt or Pt group metals (PGM) supported on metal oxides also show high activity over a wide temperature range, making them candidates for both high and low temperature operation. However, improvements are required to reduce their cost and increase stability. A novel approach has been proposed by INL and USC involving the deposition of monolayers of Pt shells on high melting temperature oxophilic cores [15]. In summary, the main challenges to developing the technology for solar decomposition of H_2SO_4 are related to catalyst performance and endurance, stability of materials of construction at elevated temperature, modeling of transient behavior, and demonstration at a relevant scale of performance during on-sun testing.

2.3 SO_2 Energy Storage

Energy storage in the form of SO_2 is required for the solar HyS plant to provide a constant 24-h H_2 output. The storage section interfaces with both the electrolyzer and the solar vaporizer/decomposer. It recovers heat from the decomposed acid stream and uses it to preheat the vaporizer feed and concentrate the acid leaving the electrolyzer system. Furthermore, SO_2 is separated from the decomposed acid and stored for reuse in the SDE. The major challenges are defining materials compatible with the process environment, optimizing heat integration, and developing cost-effective and efficient designs to separate and store large quantities of SO_2. In the baseline approach, approximately 80% SO_3 to SO_2 conversion is projected at the decomposition design point of 850°C. Thermal energy is recuperated from the decomposed stream via two heat exchangers and used to heat and evaporate the acid feed. In a third direct contact exchanger, the decomposed stream is contacted with the acid tank feed to dissolve any undecomposed SO_3. This concentrates the feed and produces a gaseous SO_2-O_2 stream at the exchanger exit. It is then compressed (~5bar) at ambient temperature so that >99% of the SO_2 can be liquefied, separated and stored. Pressurized liquid storage at 5-10 bar is the baseline approach, but SO_2 dissolved in either water or sulfuric acid will also be considered. To recover the SO_2 remnant from the O_2 stream, the gas is contacted with either water or dilute H_2SO_4. The efficacy of this scrubbing step as a function of acid concentrations and temperatures will be determined via laboratory experiments.

2.4 SO_2 Preliminary Performance and Cost Estimates

As presented above, the technical feasibility of the Solar HyS plant has been established at lab-scale for the major systems. Additional performance improvements are the target of the team's efforts. The capability to achieve the cost and performance targets at large scale can be projected based on extensive plant design studies and cost analyses conducted in conjunction with industry experts and technical specialists. For example, a study by SRNL, Westinghouse and Shaw [16] reported the cost of H_2 from a conservatively designed nuclear HyS plant to be \$5.34-\$6.18/kg, whereas the DOE final report on the STCH program by TIAX showed an estimated solar H_2 cost projection of \$3.85/kg, the second lowest of the thermochemical cycles studied. An updated process performance assessment and H2A cost-of- H_2 projection have been performed for this effort. The basis for the estimate is a HyS plant located in the southwestern U.S. with a single power tower for acid vaporization/ decomposition, liquid SO_2 storage, and an electrolyzer designed for continuous operation. The design plant capacity is 50 TPD H_2. The solar vaporizer/decomposer is designed with a solar multiple of 2.7, yielding a 76% plant capacity factor based on 16 h of chemical storage. Electricity is assumed to be purchased from an adjacent solar electric plant or the grid. Assumed performance values for each of the major process sections are shown in Table 1. The projected HyS solar-to- H_2 efficiency exceeds the technical targets established in the MYRDD plan.

Table 1. Performance Efficiency Assumptions

Process Unit	2015	2020	Comments
Heliostat Field Efficiency	45%	55%	SunShot goals for 2020
Solar Receiver	85%	90%	SunShot goals for 2020
Acid Decomposition System	70%	80%	Based on SRNL Aspen Plus™ flowsheet
Solar Electric Generation	15%	22%	CY2020 assumes Brayton cycle
Electrolyzer Efficiency	42%	70%	Voltage = 700 mV (2015) 500 mV (2020)
Solar-to- H_2 Energy Conversion Ratio	11.2%	20.2%	Based on all solar input, including electricity

Preliminary H2A v3 cost analyses were performed for years 2015 and 2020. The analysis was based on detailed estimates of capital cost and installation factors developed by several sources during previous studies funded by the DOE-NE and DOE Office of Energy Efficiency and Renewable Energy (EERE), as well as other sources. Modifications and refinements in the cost estimate for the solar version of HyS have been made based on engineering judgments. The H2A results show a projected cost of H_2 for years 2015 and

2020 of \$6.21/kg and \$3.11/kg, respectively. For 2020, the capital costs contribute 57% to the cost of H_2, fixed O&M contributes 16%, while variable costs (primarily the cost of electricity) contribute 27%. The largest contributors to the capital cost are the heliostat field (44%), the acid handling/separation system (24%), electrolysis system (11%), and SO_2 and acid storage (8%). Several additional process improvements and cost reductions are possible that could permit a Solar HyS plant to achieve the MYRDD's ultimate cost-of-H_2 goal of \$2.00/kg. These include further reductions in heliostat costs, lower solar electricity costs, improvements and cost reductions for acid handling/separation and SO_2 storage, and higher process efficiency due to further improvements in electrolyzer performance. Increasing the H_2 plant capacity to 100 TPD would also contribute to lower product costs.

The major risk for meeting the DOE H_2 production cost goal is the ability to achieve the performance and cost reductions for the solar portion of the plant, including solar electric generating efficiency and heliostat costs. These are being addressed under the DOE SunShot program. Risks specific to the HyS plant include the reliability of the materials for the acid handling and high temperature portions of the plant, the cost and lifetime of the decomposition catalyst, and the electrolyzer performance and durability. The major goal of this team effort is to address these risks and develop solutions for overcoming them.

3. Approach

3.1 Team Objective

The team's objective is to verify technical solutions to the critical shortcomings and barriers for the Solar HyS process and to demonstrate them in an on-sun test within three years. This effort has been organized around the three main technology areas of the process plus supporting tasks. The first task consists of system design and analysis, during which the critical barriers will be identified and performance levels established to help guide the research on pathways for meeting the MYRDD goals. An assessment of the feasibility of meeting these goals will take place after the first year. The second through fourth tasks consist of research programs for the key technologies. An assessment of the likelihood of achieving proof-of-concept verification is scheduled after the second year. During the third year, a virtual plant on-sun demonstration will be performed to verify the technology solutions. A collaborative approach leveraging complimentary expertise between team members will be employed to achieve a holistic approach to solving the technical problems. This approach will include informal collaborations with other DOE and EU H_2 production projects, as well as complementary research being conducted by university partners.

3.2 Task Descriptions

3.2.1 System Design and Analysis – This task is divided into three subtasks. The first is process design and flowsheet synthesis, which addresses the overall HyS plant design and consists of the development of Aspen Plus™ process flowsheet models, material and energy balances, and calculated plant performance and efficiency. Tradeoff studies will be performed for various operating and design conditions in order to help establish performance targets and design parameters for the major process operations. The results will be used in conjunction with the H2A analysis to ensure that MYRDD goals can be achieved. An initial technical evaluation will help identify critical barriers for each major system and will provide input to the first assessment. The models will be updated periodically based on research results and process design improvements.

The second subtask addresses sulfur system properties and will involve molecular thermodynamic modeling. The solution chemistry and phase behavior of the reactive system SO_2-H_2SO_4-H_2O-SO_3-O_2 is highly complex and non-ideal, and data at high temperatures is lacking. Research will mainly be carried out using the process simulation package Aspen Plus™, the underlying thermodynamic package Aspen Properties™, and the quantum chemistry code Accelrys Materials Studio®. Texas Tech will be responsible for developing and parameterizing an electrolyte-NRTL model of the system that will be incorporated by SRNL into the full HyS Aspen Plus™ process flowsheet model.

The third subtask, techno-economic modeling, consists of using the DOE H2A analysis tool to model HyS system performance and predict cost-of-H_2 results for various scenarios. Capital cost estimates will be made for complete HyS commercial H_2 plants for year 2015 as well as 2020. Input will be received from the developers of the various major processing sections on projected performance and costs of their components. Sensitivity analyses based on the process performance results from the first subtask and the testing results for the plant process areas will be conducted and the results used to guide development efforts and identify pathways to achieving MYRDD goals. The H2A models will be updated periodically, including a final H2A at the completion of the project depicting HyS results versus the MYRDD goals.

2014 WORLD HYDROGEN ENERGY CONFERENCE 2014 whec2014.com

3.2.2 Electrolyzer Development – The goal of this task is to develop technical solutions to improve the performance, lifetime, and cost effectiveness of the SDE, including a pathway to achieving a cell voltage of 700 mV by 2015 and 500 mV by 2020. Prior to electrolyzer testing, electrocatalyst and membranes with improved properties will be developed ex-situ. Once the individual components are optimized, they will be incorporated into an MEA and tested in the button cell electrolyzer.

The first subtask will focus on electrocatalyst development. Recent studies performed at SRNL [17] indicate that combinations of PGM can increase the intrinsic activity of the current catalysts by an order of magnitude. However these experiments were performed with thin films in flat substrates. This subtask will expand and optimize the metal concentrations in the alloy to improve the electrocatalyst's activity and to verify stability. The task will concentrate on Pt and Au based alloys mixed with transition metals. Once the proper alloy components are identified, the catalysts will be prepared on high surface area supports to maximize the gravimetric specific activity. A similar approach will be used for the screening and preparation of cathode catalysts. Material composition for the cathode will be focused on Ni and Ni-Cr based alloys. Sputter deposition will be used for preparing thin alloy films of different compositions in a fast and precise fashion. Alloys will be deposited on mirror-polished corrosion resistant Ti coupons that will be installed later in an electrochemical cell to test the electrochemical activity and stability. Physical characterization of catalysts and support optimization will be carried out by monitoring the properties of the materials at all stages of the synthesis. Tests will be conducted in order to determine catalytic enhancements due to metal support interactions and catalyst-support stability. These will include evaluation techniques using inductively couple plasma (ICP), electron microscopy, and x-ray diffraction (XRD) to evaluate metal loading, catalyst microstructure and crystalline pattern, respectively. Production of catalyst nanoparticles on high surface area carbon supports will be performed using processes previously used and optimized at SRNL, including seed-mediated nanoparticle growth using $NaBH_4$ as the reducing agent [18] or through the use of polyol reduction.

Prior to SO_2 exposure, the sputtered thin film samples on the Ti coupons will be cycled electrochemically to study the surface reaction and stability of the films. SO_2 catalytic performance will be measured by linear sweep voltammetry at room temperature to study the electrolysis of bubbled SO_2 to form H_2SO_4 and H_2 in H_2SO_4 solutions. In the case of cathode catalyst testing, the H_2 underpotential deposition and H_2 evolution reaction will be measured by cycling the electrocatalysts to potentials below 0 V vs RHE (reversible H_2 electrode) in the presence and absence of known concentrations of SO_2 and H_2S. Catalysts on high surface area carbon will be tested as thin films by dispersing the catalyst powder in DI (deionized) water and ethanol solutions and by fixing them on the electrode with Nafion®. Electrochemical testing will follow as described above.

The second subtask will focus on PEM development, leveraging collaboration with USC. It will build upon procedures developed at USC for casting and doping improved PBI membranes, termed the PPA process. Sulfonated PBI (s-PBI) membranes will be prepared using the same process starting with sulfonated monomers to impart an additional acid moiety in the polymer structure to enhance conductivity. USC will focus on developing highly stable s-PBI membranes that can operate at high acid concentrations and temperature. The chemical stability of the membranes in a corrosive environment will be examined using accelerated screening methods to provide insight into the potential long-term performance. Following acid exposure, the membranes will be characterized using infrared spectroscopy to compare the spectra taken before and after the screening test to determine the impact on membrane functional groups. Membrane transport of SO_2 will be evaluated under non-polarized conditions using techniques developed at SRNL and USC. The ionic conductivity will be evaluated in the SDE button cell.

The third subtask, button-cell SDE testing, will use SRNL's existing pressurized button cell test facility to evaluate the performance of new s-PBI membranes and suitable electrocatalysts. In-house MEA preparation methods will be used and optimized to prepare catalyst coated membranes. The completed MEAs will then be assembled into single cells and tested for activity and stability according to SRNL developed protocols. Tests include polarization curves, chronopotentiometry, electrochemical impedance, and in-situ SO_2 crossover.

3.2.3 Solar System Development – This task is divided into five subtasks. The first is development of the sulfuric acid decomposer. The high temperature SO_3 decomposer portion of the two-chamber solar reactor developed by DLR, is ready for scale-up, while the evaporator needs to be redesigned in order to develop a solar tower demonstrator in the future. Therefore, DLR will construct a laboratory-scale prototype in the 10 kW

2014 WORLD HYDROGEN ENERGY CONFERENCE 2014
WHEC2014.com

range for vaporization of sulfuric acid. This evaporator will incorporate a novel and scalable design concept forming the basis of future solar tower demonstrators. DLR will perform on-sun testing with the prototype evaporator in its solar furnace/simulator in Cologne, Germany. Also, an integration concept for advanced catalysts resulting from the fifth subtask below will be developed in order to convert a substantial fraction of SO_3 in the evaporator before entering the high temperature decomposer chamber.

On-sun testing is time consuming and limited in terms of operating conditions and reactor configuration. Therefore, DLR will develop a system model of the solar sulfuric acid evaporator as the second subtask and validate it with experimental data from the solar furnace/simulator tests. Moreover, an existing and experimentally validated model of DLR's laboratory-scale SO_3 decomposer will be adapted and applied in combination with the evaporator model to simulate the performance of a two-chamber sulfuric acid cracker at the laboratory scale. Based on these results, a solar tower scale-up of this reactor concept will be developed including solar field design. The system models will be adapted to predict the performance of this scale-up in order to evaluate its feasibility for future demonstration of the technology.

For the third subtask, DLR will integrate the model of the scaled solar reactor into the process simulation to analyze the impact of the solar receiver/reactor system on H_2 production. The effect of intermittent solar input over the course of a day and a year will be of particular interest for this process simulation. In this context, DLR will develop control procedures for operating the solar receiver to optimize the performance of the receiver/reactor system and the process as a whole. Moreover, DLR will evaluate the costs of the solar receiver/reactor as part of a techno-economic assessment of the H_2 production plant.

Testing of materials of construction for the acid cracking step comprises the fourth subtask. During decomposition of H_2SO_4, the vaporization step is particularly corrosive. In long-term testing, silicon carbide was found to withstand the harsh conditions during the phase change from liquid to gaseous acid over several thousand hours. However, metals have significant advantages as construction material in terms of flexibility and manufacturing. In order to introduce metallic components in an evaporator for sulfuric acid, the corrosion resistance needs to be enhanced by suitable alloying components or protective coatings. DLR will perform a screening analysis of advanced metals and carry out long term corrosion testing in boiling sulfuric acid with selected samples for up to 5,000 h to prove their feasibility.

The fifth subtask is development of a decomposition catalyst. As mentioned previously, copper vanadate based materials showing promising SO_3 conversion capability in the low temperature range (down to 600°C) have been developed. Based on these findings, the Aerosol and Particle Technology Laboratory (APTL) in Greece will be subcontracted to synthesize candidate catalyst materials for SO_3 reduction at 600-700°C and measure their initial activity. For selected catalysts, DLR will carry out durability testing for up to 1,000 h to demonstrate stability during decomposition of SO_3. APTL will perform physico-chemical analyses with the tested samples applying qualified measuring techniques like scanning electron microscope/energy dispersive x-ray (SEM/EDX) analysis, XRD, and thermal gravimetric analysis (TGA). In an alternative approach, INL and USC will synthesize and test bimetallic core/shell catalysts for high temperature operation. Pt and PGM-based monolayer shells will be deposited on high melting, oxophilic base metals such as Ru, Ni, Co or Re cores using electroless deposition techniques. These enhanced materials are expected to have high activity, superior stability, and lower cost than traditional metal oxide supported Pt based catalyst. Electroless deposition will also be used to prepare catalysts having controlled, bimetallic surfaces, such as Au-Pt, to test whether such compositions have superior activities to permit operation at temperatures lower than those currently used. These materials will also be tested for durability for up to 1,000 h and will be examined by a variety of physico-chemical methods.

3.2.4 Acid/SO_2 System Development – This task ask is divided into four subtasks, starting with flowsheet design and economic assessment. A process flowsheet for pre- and post-acid decomposition management will be established. Heat recuperation between various fluid streams will be optimized. The process window for the baseline SO_3 recycling, SO_2-O_2 separation and SO_2 storage approaches will be defined. Using the flowsheet design, an economic assessment to minimize the operating cost as a function of process parameters will be carried out. The design of the bench scale system will be based on the requirements outlined in the flowsheet. Upon completion of bench top testing, the resulting data will be incorporated in the final flowsheet design.

The second subtask is laboratory verification of the baseline separation and process designs. The extent of SO_3 recycling and SO_2-O_2 separation as predicted by the

2014 WORLD HYDROGEN ENERGY CONFERENCE 2014
whec2014.com

flowsheet will be experimentally verified. Solubility of SO_3 and SO_2 in various concentrations of H_2SO_4 as a function of temperature will be determined. Results will be used to update the process conditions in the flowsheet and system economics.

Design, construction and testing of the bench-scale system comprise the third subtask. Based on the flowsheet process parameters, a bench scale unit for SO_2 separation and storage will be designed, constructed and tested. The unit will be sized to meet or exceed the 3-L H_2 target required for system integration testing (Section 3.2.5). It will be built using proper materials of construction and designed to allow scale-up for larger demonstrations. The unit will be tested under conditions that simulate the process window specified in the flowsheet, and the results will be used to validate the flowsheet design and project economics. In parallel, a quartz-based acid concentration system will be constructed to enable acid concentration to be performed during integrated testing.

The fourth subtask is design of a full commercial scale unit. Based on the bench scale unit test results, a scaled up model design of the system and an assessment of the economics of the process unit will be conducted.

3.2.5 Acid/SO_2 Virtual Plant On-sun Demonstration – The objective of this task is to demonstrate the full HyS process by conducting a "virtual" plant demonstration near the end of the project. This will be a coordinated test where common interface conditions will be maintained between all three major process systems. The solar acid decomposition system will be tested on-sun at DLR in its solar furnace/simulator in Cologne, Germany; the SDE will be tested at SRNL; and the acid/SO_2 system will be tested at GA. Simulated integrated operation will be achieved by matching interface conditions between systems and utilizing the system simulation models. The on-sun test will be conducted for $\geq$ 8 h and the electrolyzer will be operated to produce $\geq$3 L H_2.

4. Summary

An international team has been assembled to develop a virtual demonstration of a solar HyS cycle process. Led by SRNL, the team intends to verify technical solutions to barriers for a solar HyS process and to demonstrate them in an on-sun test within three years. This effort has been organized around the three primary areas of the process as well as supporting tasks. The primary process components include the SDE, the solar acid decomposition reactor, and the SO_2 separation and acid handling system, and the team members responsible for their development are SRNL, DLR, and GA, respectively. The other three partners will help develop improved catalysts (INL and USC) and membranes (USC), as well as a properties model for the highly non-ideal SO_2-H_2SO_4-H_2O-SO_3-O_2 system. SRNL will be responsible for the overall system design and analysis, which will identify critical barriers and performance levels to help guide the research toward meeting the MYRDD goals. During the third year, a virtual plant on-sun demonstration will be performed to verify the technology solutions. Integrated operation will be simulated by matching interface conditions between systems and using process models to demonstrate that the components will work together as needed. Based on these results, a detailed commercial scale solar HyS plant design will be prepared and used to estimate the cost of hydrogen production.

Acknowledgements

The authors wish to acknowledge the financial support of DOE EERE. SRNL is operated for the DOE's Office of Environmental Management by Savannah River Nuclear Solutions, LLC under contract number DE-A C09-08SR22470.

REFERENCES

[1] Gorensek MB, Summers WA. "Chapter 18, The hybrid sulfur cycle," in *Nuclear Hydrogen Production*. Hino R, Yan XL, eds. Boca Raton, FL: CRC Press, (**2011**) 499-545.

[2] Kromer M, Roth K, Takata R, Chin P. Support for cost analyses on solar-driven high temperature thermochemical water-splitting cycles; Final report to: Department of Energy (**2011**), TIAX, LLC Reference D0535.

[3] Summers WA. Hybrid Sulfur Thermochemical Process Development. *2008 Annual Merit Review Proc; Hydrogen Prodn and Delivery*. June 12, **2008** (http://www.hydrogen.energy.gov/pdfs/review08/pd_26_summers.pdf).

[4] Colón-Mercado HR, Hobbs DT. Catalyst evaluation for a sulfur dioxide-depolarized electrolyzer. *Electrochem Comm*. **2007**; 9: 2649-53.

[5] O'Brien JA, Hinkley JT, Donne SW. Electrochemical Oxidation of Aqueous Sulfur Dioxide II. Comparative Studies on Platinum and Gold Electrodes. *JECS*. **2012**; 159(9): F585-93.

[6] Elvington MC, Colón-Mercado H, McCatty S, Stone SG, Hobbs DT. Evaluation of proton-conducting membranes for use in a sulfur dioxide depolarized electrolyzer. *J Power Sources*. **2010**; 195: 2823-9.

20th WORLD HYDROGEN ENERGY CONFERENCE 2014
whec2014.com

[7] Jayakumar JV, Gulledge A, Staser JA, Kim C-H, Benicewicz BC, Weidner JW. Polybenzimidazole Membranes for Hydrogen and Sulfuric Acid Production in the Hybrid Sulfur Electrolyzer. *ECS Electrochem Lett*. **2012**; 1(6): F44-8.

[8] General Atomics. Decomposition of Sulfuric Acid Using Solar Thermal Energy. General Atomics Report No. GA-A17573 (**1985**); General Atomics. High-Pressure Catalytic Metal Reactor in a Simulated Solar Central Receiver. General Atomics Report No. GA-A18285 (**1986**).

[9] Kolb GJ, Diver RB, Siegel N. Central-Station Solar Hydrogen Power Plant *J Sol Energy Eng*. **2007**; 129(2): 179-83.

[10] Le Duigou A, Borgard J-M, Larousse B, Doizi D, Allen R, Ewan BC, et al. HYTHEC: An EC funded search for a long term massive hydrogen production route using solar and nuclear technologies. *Int J Hydrogen Energy*. **2007**; 32(10-11): 1516-29.

[11] Roeb M, Thomey D, Graf D, Sattler C, Poitou S, Pra F, et al. HycycleS: a project on nuclear and solar hydrogen production by sulphur-based thermochemical cycles. *Int J Nucl Hydrogen Prod Appl*. **2011**; 2(3): 202-26.

[12] Thomey D, de Oliveira L, Säck J-P, Roeb M, Sattler C. Development and test of a solar reactor for decomposition of sulphuric acid in thermochemical hydrogen production. *Int J Hydrogen Energy*. **2012**; 37(21): 16615-22.

[13] Karagiannakis G, Agrafiotis CC, Pagkoura C, Konstandopoulos AG, Thomey D, de Oliveira L, et al. Hydrogen production via sulfur-based thermochemical cycles: Part 3: Durability and post-characterization of silicon carbide honeycomb substrates coated with metal oxide-based candidate catalysts for the sulfuric acid decomposition step. *Int J Hydrogen Energy*. **2012**; 37(10): 8190-203.

[14] Machida M, Kawada T, Hebishima S, Hinokuma S, and Takeshima S. Macroporous Supported Cu–V Oxide as a Promising Substitute of the Pt Catalyst for Sulfuric Acid Decomposition in Solar Thermochemical Hydrogen Production. *Chem Mater*. **2012**; 24(3): 557-61.

[15] Rebelli J, Rodriguez AA, Ma S, Williams CT, Monnier JR. Preparation and characterization of silica-supported, group IB–Pd bimetallic catalysts prepared by electroless deposition methods. *Catal. Today*. **2011**; 160(1): 170-8.

[16] Gorensek MB, Summers WA, Bolthrunis CO, Lahoda EJ, Allen DT, Greyvenstein R. Hybrid sulfur process reference design and cost analysis. Savannah River National Laboratory, Report No. SRNL-L1200-2008-00002, June 12, **2009** (doi: 10.2172/956960).

[17] Summers WA, Colón-Mercado HR, Weidner JW. Electrolyzer Component Development for the HyS Thermochemical Cycle. *2013 Annual Merit Review Proc; Hydrogen Prodn and Delivery* May 15, **2013** (http://www.hydrogen.energy.gov/pdfs/review13/pd096_summers_2013_p.pdf).

[18] Hunyadi Murph SE, Murphy CJ, Colón-Mercado HR, Torres RD, Heroux KJ, Fox EB, et al. Tuning of size and shape of Au–Pt nanocatalysts for direct methanol fuel cells. *J Nanoparticle Res*. **2011**; 13: 6347-64.

20th WORLD HYDROGEN ENERGY CONFERENCE 2014
whec2014.com