DEVELOPMENT OF THE HYBRID SULFUR THERMOCHEMICAL CYCLE

William A. Summers and John L. Steimke
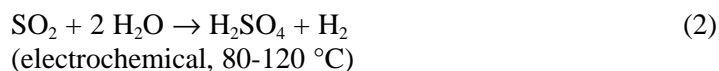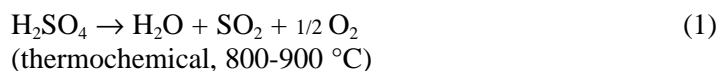Savannah River National Laboratory, USA

Abstract

The production of hydrogen via the thermochemical splitting of water is being considered as a primary means for utilising the heat from advanced nuclear reactors to provide fuel for a hydrogen economy. The Hybrid Sulfur (HyS) Process is one of the baseline candidates identified by the U.S. Department of Energy [1] for this purpose. The HyS Process is a two-step hybrid thermochemical cycle that only involves sulfur, oxygen and hydrogen compounds. Recent work has resulted in an improved process design with a calculated overall thermal efficiency (nuclear heat to hydrogen, higher heating value basis) approaching 50%. Economic analyses indicate that a nuclear hydrogen plant employing the HyS Process in conjunction with an advanced gas-cooled nuclear reactor system can produce hydrogen at competitive prices. Experimental work has begun on the sulfur dioxide depolarized electrolyzer, the major developmental component in the cycle. Proof-of-concept tests have established proton-exchange-membrane cells (a state-of-the-art technology) as a viable approach for conducting this reaction. This is expected to lead to more efficient and economical cell designs than were previously available. Considerable development and scale-up issues remain to be resolved, but the development of a viable commercial-scale HyS Process should be feasible in time to meet the commercialisation schedule for Generation IV gas-cooled nuclear reactors.

Introduction

U.S. President George W. Bush has established the Hydrogen Fuel Initiative to ensure the nation's long-term energy security and a clean environment. To this end, the U.S. Department of Energy (DOE) is exploring clean hydrogen production technologies using fossil, nuclear and renewable resources to revolutionize the way we power cars, homes and businesses. The DOE Office of Nuclear Energy, Science and Technology has established the Nuclear Hydrogen Initiative (NHI) to develop the technologies that can most effectively be coupled to next generation nuclear reactors for hydrogen production. The NHI R&D plan [2] identifies sulfur-based thermochemical cycles and high temperature steam electrolysis as the leading approaches. Thermochemical cycles produce hydrogen through a series of chemical reactions that result in the splitting of water, with all other chemical species regenerated and recycled within the process. Overall thermal efficiencies approaching 50% are possible for converting the heat from the nuclear reactor to hydrogen chemical energy (higher heating value basis) using thermochemical cycles.

The Hybrid Sulfur (HyS) Process is one of the two baseline thermochemical cycles identified for development in the NHI program. (The sulfur-iodine cycle is the other). HyS is an all-fluids, two-step hybrid thermochemical cycle, involving a single thermochemical reaction and a single electrochemical reaction. The chemical reactions are shown below:

$$H_2SO_4 \rightarrow H_2O + SO_2 + 1/2\,O_2 \qquad\qquad\qquad (1)$$
(thermochemical, 800-900 °C)

$$SO_2 + 2\,H_2O \rightarrow H_2SO_4 + H_2 \qquad\qquad\qquad (2)$$
(electrochemical, 80-120 °C)

The net result of the two reactions is the decomposition of water into hydrogen and oxygen. Since the chemistry involves only sulfur, oxygen and hydrogen compounds, many of the development issues associated with more complex thermochemical processes, such as cross-contamination and halide-induced stress corrosion cracking, are eliminated.

In recent years the sulfur-iodine thermochemical cycle has received considerable attention in development programmes in the United States, Japan, France and elsewhere [3,4]. The HyS Process, however, has seen little research since the early 1980s. The goals of the research programme at SRNL were to perform a conceptual design analysis of the process, identify major technical issues and challenges, and initiate development of the electrolyzer.

Background

The Hybrid Sulfur Cycle, also known as the Westinghouse Sulfur Cycle or the Ispra Mark 11 Cycle, was originally proposed and investigated by Westinghouse Electric Corporation in the 1970s [5,6]. All basic chemistry steps were successfully demonstrated. By 1978, a closed-loop, integrated laboratory bench-scale model was successfully operated producing 120 liters (STP) of hydrogen per hour. Work continued on equipment design and optimisation, materials of construction, integration with a nuclear/solar heat source, process optimisation, and economics until 1983. However, the general decline of support for alternative energy programs, combined with reduced interest in developing either advanced nuclear reactors or high-temperature solar receivers, led to the termination of the work on this promising process.

All sulfur-based thermochemical cycles have a common oxygen-generating, high temperature step (Reaction 1). This is an equilibrium reaction, which is carried out over a catalyst at 800 to 900 °C. It is highly endothermic, and accounts for the primary input of high temperature heat. In the case of a nuclear hydrogen plant, this heat is supplied by a hot secondary helium stream that is heated in an intermediate heat exchanger by primary helium used to cool the nuclear reactor. In reality the acid decomposition process involves multiple processing steps, including preheating, acid concentration, acid vaporisation, acid dissociation, and sulfur trioxide decomposition. The processing environment is highly corrosive, requiring super alloys or non-metallic components. Considerable work is being done on the acid decomposition process in relationship to the sulfur-iodine process development, and this can be directly applied to the HyS cycle.

The unique aspect of the HyS Process is the use of an electrochemical step (Reaction 2) to convert sulfur dioxide back to sulfuric acid and to generate hydrogen. Sulfur dioxide is oxidized at the anode of an electrochemical cell, while protons are reduced at the cathode to produce hydrogen. The presence of sulfur dioxide depolarises the anode and reduces the reversible (theoretical minimum) voltage relative to that required for the direct dissociation of water into hydrogen and oxygen. Whereas at 25°C direct water dissociation by electrolysis requires a reversible cell voltage of 1.23 volts, the sulfur dioxide depolarised electrolyzer (SDE) requires a reversible voltage of only 0.17 volts per cell. Dissolving the SO_2 feed in 50 wt% sulfuric acid increases the reversible cell voltage to 0.29 volts [7]. Actual performance, including ohmic losses and reaction irreversibilities, is expected to be approximately 0.60 volts per cell. This is significantly less than the performance of commercial direct water electrolysers that operate with 1.8 to 2.6 volts per cell [8]. Therefore, an SDE requires substantially less electricity than a conventional electrolyzer for the same hydrogen output. When combined with the endothermic decomposition of H_2SO_4, the net thermal efficiency for water-splitting by the HyS process is 30-50% higher than that for a process consisting of all electric production followed by direct water electrolysis, even when highly efficient gas-cooled nuclear reactors using a Brayton Cycle are used for electrical energy generation.

The current work by SRNL included the creation of high-efficiency process design for the HyS Process. A block flow schematic for the process is shown in Figure 1. Since HyS is a hybrid thermochemical cycle, energy input in the form of both electricity and thermal energy is required. For a commercial nuclear hydrogen plant, approximately 38% of the nuclear reactor thermal output would be directed to electricity production and 62% to provide process heat.

Figure 1.   Hybrid Sulfur Process Block Schematic
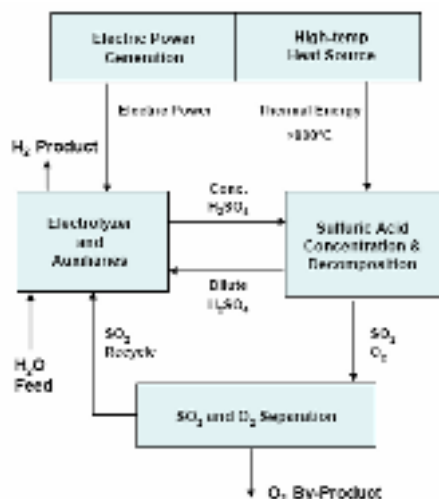
Significant improvements were realized in several processing sections compared to previous work performed by Westinghouse Electric. A baseline plant thermal efficiency for a commercial nuclear hydrogen plant of 48.8% was calculated. The efficiency was based on the higher heating value (HHV) of the hydrogen product divided by the total thermal energy output of the nuclear reactor, including the thermal energy used to generate electricity and allowances for auxiliaries such as pumps, compressors and cooling towers. Higher thermal efficiencies, exceeding 50% HHV-basis, are deemed feasible for plants based on further optimised process flowsheets.

An economic analysis was performed to determine the projected cost of hydrogen from an integrated N^{th}-of-a-kind plant consisting of an advanced helium-cooled nuclear reactor and the HyS thermochemical process. The hydrogen production cost for the base case was $1.60 per kilogram at the plant gate. The hydrogen production cost ranged from $1.49 to $1.77 per kilogram for low and high estimates for the capital cost of the electrolyser system, the major component with the greatest cost uncertainty. The inclusion of by-product credits for oxygen production lowered the baseline cost to $1.31 per kilogram. Hydrogen costs at this level are very competitive with costs projected for other means of hydrogen production, including steam reforming of methane, coal gasification with CO_2 sequestration, and renewable energy processes. It is cautioned, however, that estimates for production costs can vary widely dependent on the underlying assumptions. A revised cost analysis using a recent standardized DOE approach to determining hydrogen costs is warranted. More discussion of the systems design and economic analysis performed for the HyS Process can be found in a recent technical paper on this subject [9]. The balance of the current paper will describe the development of the sulfur dioxide depolarised electrolyser and the experimental results.

Concept Definition

The key component in the HyS Process is the sulfur dioxide depolarized electrolyzer (SDE). In order for HyS to be a viable thermochemical cycle, the SDE must be efficient and cost effective. The process design and economic analyses discussed above indicate that an SDE should perform with a voltage of <600 mV per cell. The current density should be high in order to minimise the size and capital cost of the electrolyzer system. The final selection of operating current density will be a tradeoff between performance and capital cost and will be influenced by the cell's polarization characteristics (V vs. I) and the unit capital costs ($ per square meter of active cell area). Initial estimates indicate that a current density of 500 mA/cm^2 with electrolyser operating conditions of 100°C and 20 bar will be required for commercial systems. The goal of the SRNL electrolyzer programme is to develop an SDE using PEM cell technology that satisfies these design requirements. PEM cell technology is being developed for automotive fuel cells and onsite hydrogen generators, and cost reductions and performance improvements developed for these applications are expected to lead to similar improvements for the HyS application.

Previous SDE development by Westinghouse Electric [10] utilised a two-compartment, flow-through parallel plate cell with a porous rubber diaphragm separating the reaction compartments. The half-cell reactions are as follows:

Anode: SO_2 (aq) + 2 H_2O (aq) $\rightarrow$ H_2SO_4 (aq) + 2 H^+ + 2 e^- (3)

Cathode: 2 H^+ (aq) + 2 e^- $\rightarrow$ H_2 (g)   (4)

The anode reaction results in the greatest irreversibility, and Westinghouse tested various electrocatalysts, including palladium and platinum. The majority of research has employed platinum electrocatalyst, but this is an area of research that requires further investigation. The Westinghouse

cell utilised separate liquid streams fed to the anode and cathode compartments of the cell. The anolyte consisted of a solution of sulfuric acid, water and dissolved sulfur dioxide. The catholyte consisted of sulfuric acid and water. Sulfuric acid concentrations were similar in both streams and were varied between 30 and 70 wt%. The rubber diaphragm served to allow hydraulic communication between the two parallel flow channels. A slight positive pressure differential between the catholyte to the anolyte channels was imposed to minimise SO_2 crossover to the cathode, while still allowing the diffusion of hydrogen ions (protons) from the anode to the cathode.

The PEM cell design chosen for the current work employs a significantly different geometry than the Westinghouse cell. The PEM electrolyzer consists of a membrane electrode assembly (MEA) inserted between two flow fields. Behind each flow field is a back plate, copper current collector and stainless steel end plates. The MEA consists of a Nafion proton-exchange-membrane with catalyst-coated gas diffusion electrodes bonded on either side.

Experimental Procedure

Test Facility

A test facility for testing SO_2-depolarized electrolysers was designed and constructed. The facility was located in a large chemical hood as shown in Figure 2. A 100 lb. cylinder of sulfur dioxide is shown on the left. To the right of it is the SO_2 Absorber. In the upper middle of the picture is the electrolyser cell. Below it is the anolyte flowmeter, and below that is the anolyte pump. Further to the right is the hydrogen collector. Air flow was maintained whenever hydrogen or sulfur dioxide was present in the hood. The hood was effective, no sulfur dioxide odor leaked out.

Figure 2.   Electrolyzer Test Facility.

The cathode side of the electrolyser being tested was connected to the hydrogen handling side of the facility. For safety purposes, a pressure relief valve was connected to the hydrogen outlet of the electrolyser. There are two backpressure regulators. The first one controls the pressure in the sulfur dioxide absorber on the anode side of the cell. The absorber is used to dissolve sulfur dioxide gas in

either water or solutions of sulfuric acid and water to form anolyte. The absorber column is packed with Raschig Rings and operates in countercurrent operation; anolyte flows into the top and sulfur dioxide gas flows upward. Below the packed bed is a reservoir for approximately one liter of anolyte. An excess of sulfur dioxide gas was fed to the absorber, and the excess gas was vented. Anolyte is pumped out the bottom of the absorber, through a flowmeter, through the anolyte side of the electrolyser and back into the top of the absorber. All tubing, valves and connectors in the anolyte flow loop were made from fluorocarbon polymer (PTFE or PFA). The translucent tubing was useful in determining if lines were full of liquid or were passing a two-phase mixture. The second backpressure regulator controls the hydrogen pressure at the cathode side of the electrolyser. It is important to demonstrate the ability of the electrolyser to generate hydrogen at elevated pressures, since this will be required in commercial operation in order to reduce compressor requirements for hydrogen delivery. Downstream of the back-pressure regulator is a three-way valve that can direct product hydrogen either directly to a vent or to the hydrogen collector for flow measurement. The inner cylinder of the hydrogen collection cylinder was made from glass; an outer cylinder made from acrylic protected the glass cylinder. Upstream of the hydrogen collector is a water collection chamber with a purge valve to allow capture and sampling of any condensate that might appear.

Electrolyzer Test Units

Two different SDE's were designed, procured and tested. The first electrolyser was based on a commercially available PEM water electrolyser manufactured by Proton Energy Systems, Inc. (PES) of Wallingford, CT. The commercial-type electrolyser was built with Hastelloy B and Teflon wetted parts, a PEM electrolyte, and porous titanium electrodes. It had an active cell area of 86 cm^2, and a Pt catalyst loading of 4 mg/cm^2. SRNL requested that the titanium electrodes be changed to carbon or other more corrosive-resistant material, but they were an integral part of the commercial design and could not be modified. During testing there was evidence of severe corrosion of the metal wetted parts of the electrolyzer due to the sulfuric acid environment of the SDE.

The second electrolyser was a research unit assembled for SRNL by the University of South Carolina (USC). It was constructed with platinised carbon cloth electrodes, a Nafion 115 PEM electrolyte, carbon paper flow fields, solid graphite back plates, copper current collectors and stainless steel end plates. The USC electrolyser had an active cell area of 40 cm^2 and a Pt catalyst loading of 0.5 mg/ cm^2 (only one-eighth that of the commercial cell). The carbon-based configuration proved to be much more corrosive resistant than the commercial-type electrolyser. A photograph of the two electrolyzer units is shown in Figure 3.

Figure 3.   Photograph of the commercial-type PEM electrolyser on the left and the USC research electrolyser installed in the test facility on the right
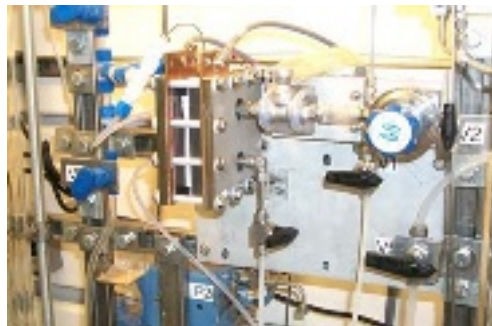
Test Procedures

The following procedure was followed preceding each test. Any previous contents of the facility were drained. A liter of the desired acid solution was mixed in a bottle. A tube was attached to the acid feed valve and inserted into the bottle of acid solution. The pump was used to draw the acid into the absorber. The acid solution was circulated through the cell and absorber at flowrates ranging from 0.3 to 1.5 liters per minute and sulfur dioxide gas was passed through the absorber at 1 liter per minute. After about 20 minutes the sulfur dioxide flow was reduced to 0.5 liters per minute and current was passed through the cell. At the end of the day of testing, the cell was drained and both sides of the cell were flushed with deionised water. The cell was filled with deionised water for overnight and weekends

The method for measuring hydrogen generation with the hydrogen collector was to displace water from an inverted cylinder positioned with its base in a shallow pool of water. This method is simple yet allows accurate measurement of low flow rates. The water temperature, hydrogen gage pressure in the inverted cylinder, and atmospheric pressure were measured to allow for volume correction. The inner cylinder of the hydrogen collection cylinder was made from glass, and an outer cylinder made from acrylic protected the glass cylinder and facilitated filling the inner cylinder with water between runs.

The power supply to the electrolyser was a Model 710 from The Electrosynthesis Company, Inc. of Lancaster NY. It was operated in constant current mode rather than in constant voltage mode. The maximum current and maximum voltage available was 50 amperes and 20 volts, respectively. In addition to current measurement provided by the power supply, a calibrated shunt was connected to the output to allow for independent measurement of current. Voltage taps independently connected to the cell electrodes were connected to the data acquisition system (DAS). The instrument signals from thermocouples, pressure gages, and flowmeters were connected to the DAS, which was comprised of a Dell computer with special acquisition boards and Labview software. Observations and some data were manually recorded in a laboratory notebook.

Results and Discussion

Plots of cell potential vs. current density, called polarization curves or Tafel plots, for the commercial-type electrolyzer are shown in Figure 4 for various anode feed conditions. Anolyte flowrate was 0.35 liters per minute; temperature was 20°C and pressure was 1.0 bar. For direct water electrolysis, the cell potential increased linearly from 1.57 volts at very low current density to 1.82 volts at nearly 600 mA/cm^2. Hydrogen production at the maximum current density was approximately 20 liters per hour. The minimum possible cell voltage is the reversible cell voltage for direct water electrolysis, which is 1.23 volts at 25°C. The excess voltage, which ranged from 0.3 to 0.6 volts, is the result of ohmic losses and various polarisations. When the cell was operated in the direct electrolysis mode (water feed only), the anolyte effluent contained a two-phase mixture of water and oxygen. When sulfur dioxide dissolved in sulfuric acid was used as the anolyte, a substantial drop in cell voltage was measured. This is the result of SO_2 depolarisation caused by the oxidation of SO_2 to H_2SO_4 at the anode in place of oxygen generation, which could be observed visibly by the absence of oxygen bubbles in the anolyte effluent.

At low current density of approximately 50 mA/cm^2, the cell voltage was 0.75 volts using 30 wt% acid. This increased to approximately 1.4 volts at near 600 mA/cm^2. These performance results were very encouraging, particularly for operation at room temperature and atmospheric pressure. However, during testing of the commercial-type electrolyser with sulfuric acid, a black liquor containing a very fine metal powder was observed. This was a result of corrosion of some of the metal components in the cell, including the titanium electrodes. Testing was then performed with 70 wt% sulfuric acid, which is

considerably more corrosive than 30 wt%. Cell potential at 50 mA/cm^2 was 0.98 volts and increased to 1.22 V at 116 mA/cm^2. Testing had to be discontinued after a short period due to excessive corrosion, including suspected loss of electrocatalyst and surface area. Unfortunately, the purchase agreement with the electrolyser supplier did not permit cell disassembly and post-test examination.

Figure 4. Polarisation Curve for Commercial-type PEM Electrolyser.
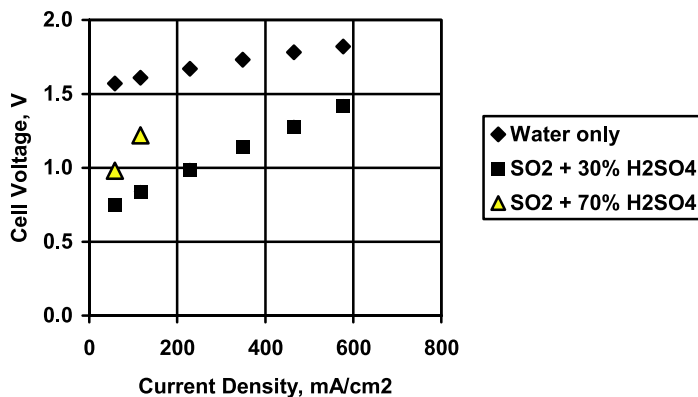
Test data for the research electrolyser provided by USC is shown in Figure 5. Tests were conducted with an anolyte feed consisting of 30 wt% sulfuric acid saturated with SO_2 at a pressure of 1 and 2 bar. The calculated concentration of SO_2 in the feed at the two pressures was 5 wt% and 10 wt%, respectively. The anolyte feederate was varied from 0.3 to 1.5 liters per minute.

Figure 5. Polarisation data for USC Research Electrolyser
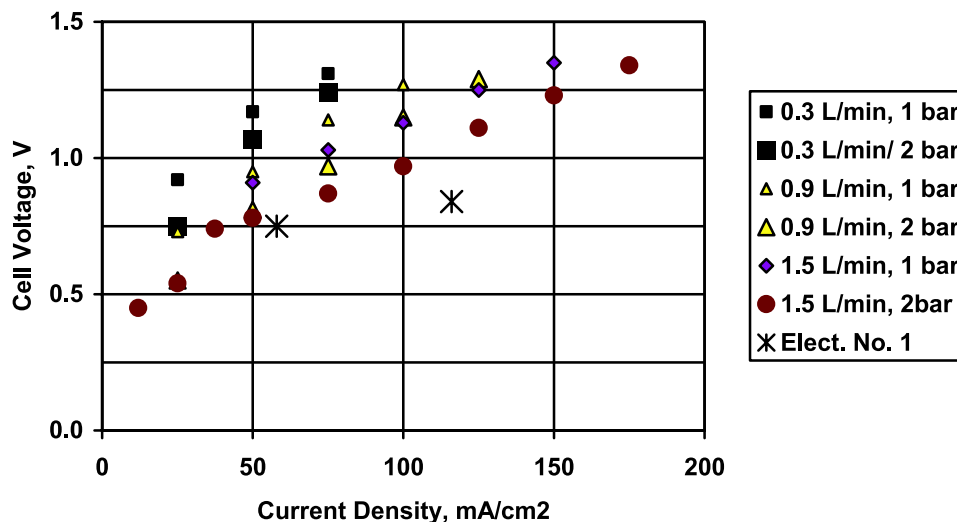
The second electrolyser achieved very good performance at low currents, with hydrogen generation occurring at a cell voltage of less than 0.5 volts at the lowest point. However, the performance indicated that the design suffered from high mass transfer resistance as evidenced by the improvement of performance with increases in anolyte flowrate. Furthermore, increasing the pressure, which increased the concentration of sulfur dioxide, had a measurable effect on reducing the voltage.

Under the highest anolyte flow and pressure conditions, the performance of the second electrolyzer was similar to that of the commercial-scale electrolyser at a modest current density

(approximately 0.75 V at 50 mA/cm^2). However, the voltage of the second electrolyser increased more rapidly with increasing current. This could partially be a result of the much lower catalyst loading in the second electrolyser. A further explanation for this behavior is likely the hydraulic design of the cells. The commercial-type cell was designed for liquid water feed, and it had relatively low fluid flow resistance and good mass transfer characteristics. The second cell was a modified design originally based on gaseous reactants, and it had poor mass transfer characteristics when using liquid sulfuric acid feed with dissolved SO$_2$. Future work will focus on improved cell designs and operation at higher temperature and pressure. The membranes in both cells permitted the passage of some sulfur dioxide from the anode to the cathode, where it reacted with hydrogen gas to form elemental sulfur. However, the sulfur did not appear to poison the cathode electrocatalyst, and it was easily washed out of the cells. Future designs should eliminate or minimise SO$_2$ crossover, or should be designed to mitigate its effects on long-term cell performance.

Conclusions

Process design analysis and preliminary economic assessments indicate that the Hybrid Sulfur Process is a viable and attractive method for utilising high-temperature heat from an advanced nuclear reactor to produce hydrogen. The key processing step that determines both the efficiency and economics of the process is the production of hydrogen using sulfur dioxide depolarised electrolysis. Proof-of-concept testing has shown that modern proton-exchange-membrane electrochemical cell designs can be utilised to conduct this reaction. Further research and cell development are necessary to establish the cell performance at commercial operating conditions and to minimize the formation of sulfur caused by diffusion through the membrane. In order to demonstrate the complete Hybrid Sulfur cycle, an integrated, closed-loop laboratory model should be constructed consisting of both the electrolyser subsystem and the sulfuric acid decomposition section.

Acknowledgements

REFERENCES

[1]   U.S. Department of Energy Office of Nuclear Energy, Science and Technology, "Nuclear Hydrogen R&D Plan", March, 2004. http://nuclear.gov/hydrogen/RandDPlan.pdf

[2]   Ibid.

[3]   Denis Doizi *et al.*, "Hydrogen Production by the Iodine-Sulphur Thermochemical Cycles: Partial Pressure Measurements", Transactions of American Nuclear Society 2005 Annual Meeting, Volume 92, San Diego, California, June 5-9, 2005.

[4]   Shinji K. *et al.*, R&D on Water Splitting IS Process for Hydrogen Production Using HTGR at JAERI, AIChE Spring National Meeting, April 25-29, 2004, New Orleans.

[5]   G.H. Farbman, "The conceptual design of an integrated nuclear-hydrogen production plant using the sulfur cycle water decomposition system", NASA Contractor Report, NASA-CR-134976, Washington, D.C., April, 1976.

[6]   Gerald H. Parker, "Solar thermal hydrogen production process", Final Report, December, 1982, to US DOE, DOE/ET/20608-1, Westinghouse Electric Corp., Pittsburgh, Pennsylvania, January 21, 1983.

[7]   Lu, P.W.T., and; R.L. Ammon, "An Investigation of Electrode Materials for the Anodic Oxidation of Sulfur Dioxide in Concentrated Sulfuric Acid," J. Electrochem. Soc.: Electrochemical Science and Technology, Vol. 127, No. 12, pp. 2610-2616, December, 1980.

[8]   Jacqueline I.Kroschwitz (executive editor), Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, John Wiley and Sons, New York, NY, c1991-c1998.

[9]   William A. Summers *et al.*, "The Hybrid Sulfur Cycle for Nuclear Hydrogen Production," Proceedings of GLOBAL 2005 , Paper 097, Tsukuba, Japan, October 9013, 2005 (in progress).

[10]   Peter W.T. Lu, "Technological Aspects of Sulfur Dioxide Depolarized Electrolysis for Hydrogen Production", *Int. J. Hydrogen Energy* **1983**, 8, 773-781.

TABLE OF CONTENTS