II.J.9 Membrane Applications for Nuclear Hydrogen Production Processes

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Objectives

- Develop inorganic membranes for the separation of SO_2 and O_2 from SO_3.
- Test membranes for stability in operational environment.
- Evaluate membranes for separation efficiency.
- Develop inorganic membranes for the separation of hydrogen from steam.
- Test membranes for separation efficiency and long term stability.
- Provide membrane separation unit for use at Idaho National Laboratory (INL).

Technical Barriers

This project addresses the following technical barriers for the Sulfur Iodine Thermochemical Cycle and the High Temperature Electrolysis projects for the Nuclear Hydrogen Initiative:

- High temperature required for sulfuric acid decomposition.
- Cool-down and reheat of steam/hydrogen stream required for separation by conventional condensation is not energy efficient.

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE systems analysis milestones from the Nuclear Hydrogen Initiative:

- Reduction of temperature for sulfuric acid decomposition step in Sulfur-Iodine (SI) Thermochemical Cycle.
- Separation of hydrogen from steam at reaction temperature to enable recycle of high temperature unreacted steam back to inlet of high temperature electrolyzer.

Accomplishments

- Demonstrated that SO_2 and O_2 have higher permeances than SO_3 through nanoporous inorganic membranes having pore-size less than 1 nm at low temperatures.
- Fabricated test system to evaluate the environmental stability of porous materials at sulfuric acid decomposition conditions.
- Designed and assembled test system to evaluate the separation of SO_2 and O_2 from SO_3 at sulfuric acid decomposition conditions.
- Formed first generation porous silicon carbide (SiC) support tubes for nanoporous membranes.
- Assembled membrane test system for the separation of hydrogen from steam at temperatures up to 800°C.
- Tested membrane at up to 450°C in steam and hydrogen for approximately 6 weeks. The membrane was leak free but the weld developed a leak.

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Introduction

Thermochemical cycles, such as those involving the decomposition of sulfuric acid (SI cycle), can facilitate the production of hydrogen from water using the heat from the next generation nuclear reactor. However, one of the reactions in the SI cycle requires temperatures of more than 850°C in order to achieve nearly complete conversion. Inorganic membranes can be used to remove the reaction products and shift the equilibrium to higher conversion at lower temperatures, which also would reduce the severity of the compatibility issues associated with these highly corrosive environments.

Approach

The Nuclear Hydrogen Initiative is investigating thermochemical cycles as methods for the production of hydrogen using nuclear energy. The baseline thermochemical cycle, SI, consists of three coupled chemical reactions. Sulfuric acid and hydrogen iodide are generated in the low temperature Bunsen reaction, and the reaction products, sulfuric acid and hydrogen iodide, are decomposed at higher temperatures. The highly endothermic (heat absorbing) gas-phase reaction in this process is:

$$2H_2SO_4 \Leftrightarrow 2H_2O + 2SO_3 \Leftrightarrow 2SO_2 + 2H_2O + O_2$$

High temperatures (more than 850°C) are required to drive the reaction to near complete conversion. There is the potential to reduce the temperature required for this sulfuric acid decomposition reaction by the use of high-temperature inorganic membranes that are selectively permeable to the desirable decomposition species. Selective removal of the sulfur dioxide and oxygen would allow the sulfuric acid decomposition reaction to proceed at temperatures as low as 700°C. Such membranes, while they have been developed and used successfully, have not been evaluated for service under the operating conditions of the SI process. Issues that need to be addressed for potential membranes include: (1) appropriateness of materials of construction with regard to high-temperature strength, corrosion resistance, and durability; (2) identification of processing parameters and resultant membrane structures most appropriate for separation of the particular desirable chemical species; and (3) assessment of separation performance under operating conditions. This project has focused on the evaluation of selected materials for inorganic membranes to determine feasibility of survival in the working environment.

Results

SI Thermochemical Cycle

A materials evaluation system was designed and constructed. An operating safety envelope for this experimental system was developed and evaluated. This safety envelope includes gas sensors/alarms for SO_2 in the hazardous gas storage cabinet and in the immediate vicinity of the test rig. The heating blanket on the cylinder of sulfur dioxide, needed to obtain an adequate flow rate of gas, is operated with temperature control limits to avoid the possibility of melting the fusible link associated with the gas cylinder. The appropriate ratio of sulfide dioxide and an argon/oxygen mixture, to establish the desired ratio of SO_2 to SO_3, is fed into the test reactor consisting of concentric quartz tubes. The gases are heated to temperature by feeding them down the annulus between the concentric tubes prior to flowing up the central tube past the specimens. The exit gas enters an absorption column to remove aggressive species before being vented to a hood. Due to clogging, the previously used solid absorption column for scrubbing the oxides of sulfur has been replaced with a flowing liquid system (Figure 1). The system consists of a column, a pump, and two 2-liter flasks furnished with drain stopcocks, which allow for replenishing of the NaOH scrubber solution as needed during testing. The lower of the two flasks (vessel 2) is fed via gravity from vessel 1. A peristaltic pump moves the solution from vessel 2 to the inlet of the scrubber column. Gravity feeds the liquid down through the column trays back into vessel 1 completing the circuit. The effluent gas enters at the bottom of the scrubber column and rises countercurrent to the solution flow and reacts with the solution. These approaches lessen the opportunity for formation of solids from reaction between gas and sodium hydroxide within narrow passages. After exposure, the specimens are evaluated microstructurally to determine reaction products and distribution of the reaction products. The combined information from the various analyses (weight change, chemical and microstructural distribution of reaction products) allow for predictions of materials' behavior at temperature and selection of more compatible materials for future evaluation.

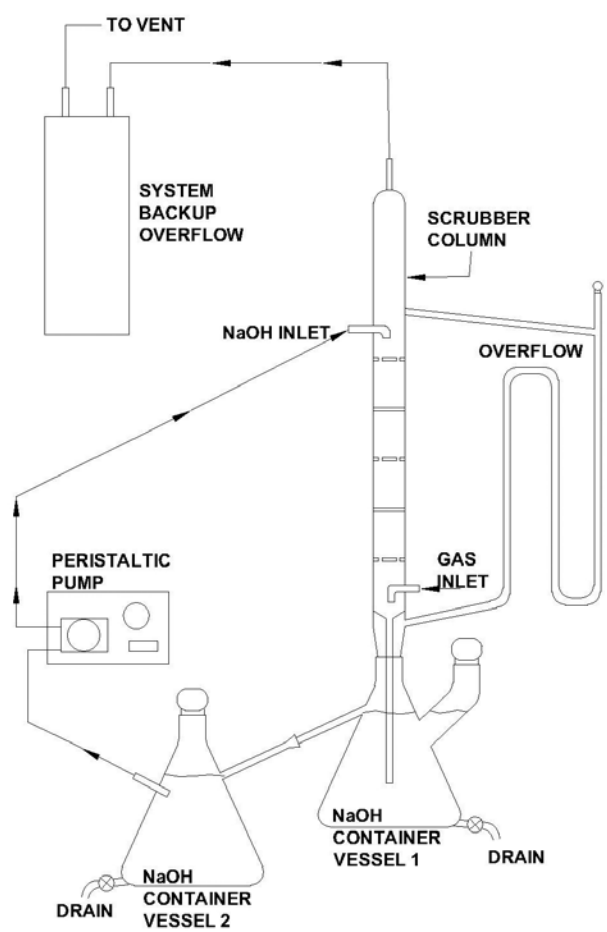

FIGURE 1. Schematic of effluent gas scrubber. An indicating dye is used to indicate consumption of scrubber solution.

While optimized silicon carbide supports were being developed in parallel to this work, porous tubes of SiC were procured for initial evaluation. These tubes are approximately 250 mm long, with an outer diameter of approximately 24 mm and a wall thickness of 6 mm. The average pore size was determined to be approximately 14 nm. Ring specimens of SiC were exposed to the sulfur dioxide and argon-oxygen gases at 550°C for 168 hours and three specimens were exposed at 900°C for 168 hours. There was also an aborted test at 935°C that completed 25 hours. Following exposure, the specimens were again measured and weighed and subjected to surface analyses.

The SiC specimens showed excellent compatibility with the reaction gases at all temperatures. Weight gains at 550°C averaged 0.14 mg/cm^2, which is significantly lower compared to the metal alloys tested previously. The weight gain corresponds to a rate of $9.6x10^{-9}$ $mgcm^{-2}S^{-1}$. The material also shows dimensional stability and did not appear to increase in brittleness. The SiC specimens tested at 900°C for 168 hours showed an average weight gain of 0.71 mg/cm^2, which corresponds to a rate of $1.17x10^{-6}$ $mgcm^{-2}S^{-1}$ and again, is significantly less than that obtained for the alloys tested at 550°C.

Initial surface analyses of specimens tested at 900°C for 168 hours showed very little sulfur products, which correlates with the low mass gain. A typical surface is presented in Figure 2. As shown, the typical surface is composed of silicon, carbon and oxygen. The white areas appear brighter when using a back scatter detector. This brightness, indicative of a lighter element, is shown in the energy map (Figure 3) to be high in oxygen. The white areas are a mixture of iron oxide and iron sulfide. Further analyses of the as-received SiC are needed to determine impurity levels.

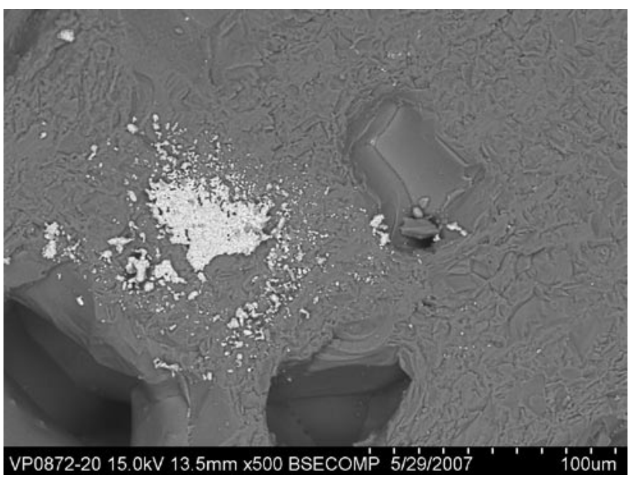

FIGURE 2. Micrograph shows SiC surface after 168 hours at 900°C. Using a back scatter detector, the white areas appear brighter.

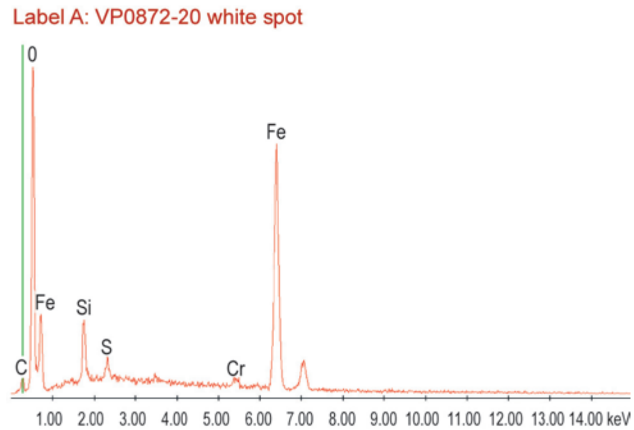

FIGURE 3. The Brighter Areas of the Micrograph are Indicative of Lighter Elements as White Area is Shown in Energy Map to be High in Oxygen

Membrane for Hydrogen/Steam Separation for High Temperature Electrolysis (HTE)

A test system was designed and fabricated to test the separation of hydrogen from a mixture of hydrogen and steam at temperatures up to 800°C. The membrane holder is heated using a tube furnace with the tubing, valves, and instrumentation heated by heat-tape to prevent condensation of water within the system. The pressure and relative humidity are monitored with sensors capable of operating at over 100°C. The hydrogen is metered into the system using a mass flow controller and the water is metered in as liquid water using a metering piston pump. The liquid water is vaporized using a small tube furnace. The mixture of hydrogen and water vapor is fed into the inside of the membrane holder.

Membrane prototypes were fabricated by applying a thin ceramic layer, having a pore size of approximately 7 nm, onto a porous stainless steel support tube. One membrane was evaluated in the test system for over six weeks at temperatures up to 450°C. During testing, a leak was detected and it was determined by external leak testing to be a defect in one of the welds between the porous support tube and the endfitting. A new membrane using a different weld treatment was installed into the system for the next phase of testing.

Conclusions and Future Directions

- SiC is the leading candidate for material of construction for the membrane support.
- Commercial porous SiC tubes showed excellent compatibility for a sulfuric acid decomposer environment.
- Fabrication of optimized SiC support tubes was successfully completed.

- Membranes for hydrogen steam separation for HTE tested at 450°C for over 40 days.
- Work in FY 2008 will concentrate on evaluating the corrosion resistance of completed SiC supported membranes.
- These completed membranes will be evaluated for separation efficiency under conditions similar to those expected to be encountered in the sulfuric acid decomposer.
- A membrane was evaluated for over 40 days at up to 450°C in the HTE test system. The membrane was found to have a leak in a weld but the membrane pore structure was not measurably changed.
- In FY 2008, a membrane will be evaluated for 1,000 hours at temperatures up to 800°C and membranes will be provided to INL for evaluation in their lab-scale test system.

FY 2007 Publications/Presentations

1. Inorganic Membranes to Facilitate the Production of Hydrogen Using Nuclear Energy, Brian L. Bischoff, Dane F. Wilson, Adam Willoughby, Lawrence E. Powell, and K. Dale Adcock. Presented at the 2006 Fall Meeting of the American Institute of Chemical Engineers, San Francisco, CA, November 13, 2006.