

August 4, 1999

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Subject: Final Topical Report for "Hydrogen Separation Membranes" – Task 6.2
DOE Contract No. DE-FC26-98FT40320; UND Fund 4410

Please find enclosed one copy of the final topical report for the subject project. A draft copy was submitted to the performance monitor on May 3, 1999. No changes were required; therefore, we are enclosing the final report with the Request for Patent Clearance for Release of Contracted Research Documents and the electronic copy on diskette.

If you have any questions regarding this submittal, please call me at (701) 777-5124, fax at (701) 777-5181, or e-mail at slandis@eerc.und.nodak.edu.

Sincerely,

Sheryl E. Landis
Manager, Contracts and Intellectual Property
Business and Operations

SEL/mjj

Enclosures

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◆ Contract Agreement No.
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(412) 386-4743

A. CONTRACTOR ACTION (CONTRACTOR COMPLETES PART A. 1-5)

1. Document Title: Task 6.2 – Hydrogen Separation Membranes; Fund 4410

2. Type of Document: Technical Progress Report Topical Report Final Technical Report
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3. Date clearance needed: _____

◆4. Patent information.

Yes	No	
<input type="checkbox"/>	<input checked="" type="checkbox"/>	Is any patentable subject matter disclosed in the report?
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<input type="checkbox"/>	<input checked="" type="checkbox"/>	Are there any patent-related objections to the release of this report? If so, state the objections. _____ _____

◆5. Signed _____ Date _____
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Name & Phone No. Sheryl E. Landis (701) 777-5124

Address Energy & Environmental Research Center, PO Box 9018, Grand Forks, ND 58202-9018

B. DOE PATENT COUNSEL ACTION

Patent clearance for release of the above-identified document is granted.
 Other: _____

Signed _____ Date _____
(Patent Attorney)

◆ Must be completed by the contractor.

TASK 6.2 – HYDROGEN SEPARATION MEMBRANES

Final Report

for the period April 1, 1998, through April 30, 1999

Prepared for:

U.S. Department of Energy
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TABLE OF CONTENTS

LIST OF FIGURES	i
1.0 BACKGROUND	1
2.0 OBJECTIVES	1
3.0 STATEMENT OF WORK	2
4.0 APPROACH	2
5.0 ACCOMPLISHMENTS	3
5.1 Membrane Preparation	3
5.1.1 Thermal ZnS Coating	3
5.1.2 Chemical ZnS Deposition	3
5.1.3 Slurry ZnS Impregnation	4
5.2 Permeation Testing	4
5.3 Thermogravimetric Experiments	5
6.0 CONCLUSIONS	7
7.0 REFERENCES	8

LIST OF FIGURES

1 Schematic of the permeation test apparatus	4
2 ZnS heated in argon and hydrogen	6
3 Uptake of hydrogen on ZnS	6
4 Differential scanning calorimetry of ZnS in hydrogen	7

TASK 6.2 – HYDROGEN SEPARATION MEMBRANES

1.0 BACKGROUND

Catalytic gasification of coal to produce H₂- and CH₄-rich gases for consumption in molten carbonate fuel cells is currently under development; however, to optimize the fuel cell performance and extend its operating life, it is desired to separate as much of the inerts (i.e., CO₂ and N₂) and impurities (i.e., H₂S and NH₃) as possible from the fuel gas before they enter the fuel cell. In addition, the economics of the integrated gasification combined cycle (IGCC) can be improved by separating as much of the hydrogen as possible from the fuel gas, since hydrogen is a high-value product. Processes currently under development for accomplishing this gas separation and hot-gas cleanup involve gas separation membranes. These membranes are projected to operate at temperatures as high as 800°C and pressures up to 300 psig. Previous approaches in the literature include membranes with relatively large pores (30–50 Å), which inefficiently separate the undesired gases by operating in the Knudsen diffusion region of mass transport. Other membranes with smaller pore sizes (<5 Å) operate in the molecular sieving region of mass transport phenomena. Separation methods by dissolution of atomic hydrogen into thin metallic membranes made of platinum and palladium alloys are also being developed.

The temperatures and other gaseous species present (CO, H₂O, and H₂S) place stringent demands on potential membrane materials as a result of membrane deterioration and poisoning. A nonmetal ceramic analog of a dense-metal membrane, in which the hydrogen would dissolve into and diffuse through the membrane, appeared to be a promising approach, since ceramics are resistant to elevated temperature and chemical attack and can have high hydrogen permeability and selectivity, which are necessary for this application.

In a related previous project at the Energy & Environmental Research Center (EERC), zinc sulfide was selected as a promising membrane material, based on the known ability of hydrogen to diffuse into the analogous zinc oxide, with the sulfide form expected to be stable in a gas mixture containing hydrogen sulfide. Short-term tests indicated that ZnS thin films could be produced and were relatively stable in a reducing environment at elevated temperature. However, because of flood damage and later failure of a critical electron-beam coating instrument used to produce the thin films, no ZnS films were produced or tested during the course of this earlier project (1).

2.0 OBJECTIVES

In previous work, zinc sulfide was selected as a promising membrane material. The objective of Task 6.2 was to further characterize thin-film membrane materials of this type as well as evaluate their permeability and long-term stability in a gasification process stream atmosphere.

3.0 STATEMENT OF WORK

Based on the results of the previous project, the most promising substrate would be selected for support of the zinc sulfide membranes for further testing. Tests would be performed to determine the effect of temperature, gas composition, and membrane thickness on membrane permeability and stability. Permeation testing would be performed in a small bench-scale permeation test cell using simulated gasification atmospheres, with the membranes examined before and after testing by scanning electron microscopy.

Assuming satisfactory stability and permeability of the membranes, the most promising membrane configuration would be selected and a small membrane filter fabricated for testing in an actual gasification atmosphere using the EERC integrated bench-scale gasifier or transport development unit.

The specific deliverable would be an evaluation of the inorganic membranes for gas permeability, separation efficiency, and stability as a function of membrane properties and operating conditions.

4.0 APPROACH

A literature review suggested that the most likely chance for a successful high-temperature membrane for hydrogen separation from a gasification product stream would be a ceramic analog of a dense-metal membrane, where the hydrogen would dissolve into and diffuse through the membrane structure. Because of the presence of hydrogen sulfide in a gasifier product gas, the physical and chemical properties of sulfide compounds were examined as these were expected to be stable against hydrogen sulfate attack.

A membrane produced from zinc sulfide appeared potentially promising since this material was expected to be stable in a reducing atmosphere containing hydrogen sulfide and with a suitably high sublimation temperature of 1185°C. The inference was made from several references in the literature that zinc sulfide had the potential for selective hydrogen transport as a membrane material. The analogous zinc oxide with an excess of zinc is an *n*-type semiconductor whose character is favorable for the chemisorption of H₂ (2). Single-crystal zinc oxide conductivity is quite sensitive to and increases in the presence of hydrogen (3). This increase in conductivity has been found to be the result of hydrogen diffusing into the crystal, with the diffusion increasing with temperature (4). The hydrogen may diffuse either as interstitial protons or by a hopping mechanism after reacting with the ZnO oxygen to form hydroxide anions. Zinc sulfide, which has been less well studied, is expected to show similar properties. It is expected that ZnS hydrogen transport will occur in a nongalvanic mode, based on the information available for ZnO. However, there is the possibility that an electrical potential may assist this transport. With successful results from initial permeation tests, electrical conductivity studies would be undertaken to elucidate the transport mechanism, as well as to explore the effects of additives which are known to profoundly affect the luminescent properties of zinc sulfide (5).

5.0 ACCOMPLISHMENTS

5.1 Membrane Preparation

Zinc sulfide is a quite-refractory material which sublimates at 1185°C and is highly insoluble. These properties make formation of a membrane from this material difficult. Initially, an electron-beam vacuum coating instrument was planned to be used to produce the thin-film membranes. Extensive flood damage and subsequent failure of the high-voltage electron-beam power supply of the instrument precluded preparing ZnS films by this method.

Alternative methods were explored to produce ZnS membranes. The initial criterion for a satisfactory membrane fabrication was that the membrane would exhibit no permeability to nitrogen gas when tested in the permeation test apparatus described subsequently. Once impermeability to nitrogen was demonstrated, subsequent tests would be performed to determine the permeability to hydrogen and the stability of the membrane in a gasification atmosphere. Porous stainless steel filter frits (1" diameter, 1/16" thickness, 0.5- μ m pore size, obtained from Mott Metallurgical Corporation) were used as a backing support for the ZnS membrane fabrication attempts. Although the stainless steel filters would not withstand the corrosiveness and temperature of an actual gasification atmosphere, they provided a very robust membrane support for the fabrication and bench-scale permeation testing.

Production of a nitrogen-impervious ZnS membrane proved exceedingly difficult and was not achieved. The following fabrication methods were tried without success.

5.1.1 *Thermal ZnS Coating*

As an alternate to the electron-beam vacuum coater producing thin-film coatings of ZnS by thermal evaporation and deposition in a Dentron Vacuum DU502A, a carbon-coating instrument was tested and found to produce thin film coatings on glass slide substrates. However, it was not possible to deposit enough ZnS to seal the relatively large pores of the stainless steel backing support. To increase the amount of ZnS sublimation, attempts were made heating ZnS in a sealed-tube furnace with subsequent deposition on the steel substrate. This was also unsuccessful.

5.1.2 *Chemical ZnS Deposition*

Chemical precipitation of a ZnS membrane on and into a sintered stainless steel substrate was tried to seal the porous substrate against nitrogen. Several application techniques, including alternate impregnation of the substrate with 1 M zinc nitrate and 1 M sodium sulfide while drawing the solutions through the steel substrate were used without success. Although the filter became blocked to the aqueous solutions being drawn through, after drying there was no perceptible reduction in porosity to nitrogen gas. Subsequent heating of the treated steel substrate to sublime and redeposit ZnS within the substrate also had no effect.

5.1.3 Slurry ZnS Impregnation

A ZnS powder slurry in ethyl alcohol was drawn into the substrate using the substrate as a filter. Variations of this preparation method included subsequent heating of the impregnated substrate to resublime and redeposit the ZnS within the substrate, pressing of the ZnS slurry surface layer after drying at 8000 psi, and pressing followed by heating. None of these techniques was successful in sealing the substrate against nitrogen.

5.2 Permeation Testing

The methods tested for producing a ZnS membrane impervious to nitrogen gas having proved unsuccessful, two 13-mm-diameter by 2-mm-thick ZnS infrared sample windows were purchased from International Crystal Laboratories. These monolithic windows provided a nitrogen-impervious barrier to allow permeation testing of a ZnS barrier with hydrogen. Because of their significant thickness, one of the windows was cross-sectioned and polished to provide a thinner 13-mm-diameter by 0.2-mm-thick ZnS “membrane.”

A schematic of the permeation test apparatus is shown in Figure 1. The design of the device was based on the instrument used by Barrer (6) and by the ASTM standard test method for determining gas permeability of plastic films (7). The permeation device is constructed from stainless steel with two capped sections of tubing connected by a bulkhead compression fitting. The section of tubing at the gas inlet side presses the membrane mounted between two vitron “o” rings against the seat of the fitting, forming a gastight seal. The compression fittings allow the apparatus to be easily disassembled for insertion and removal of test membranes, and the

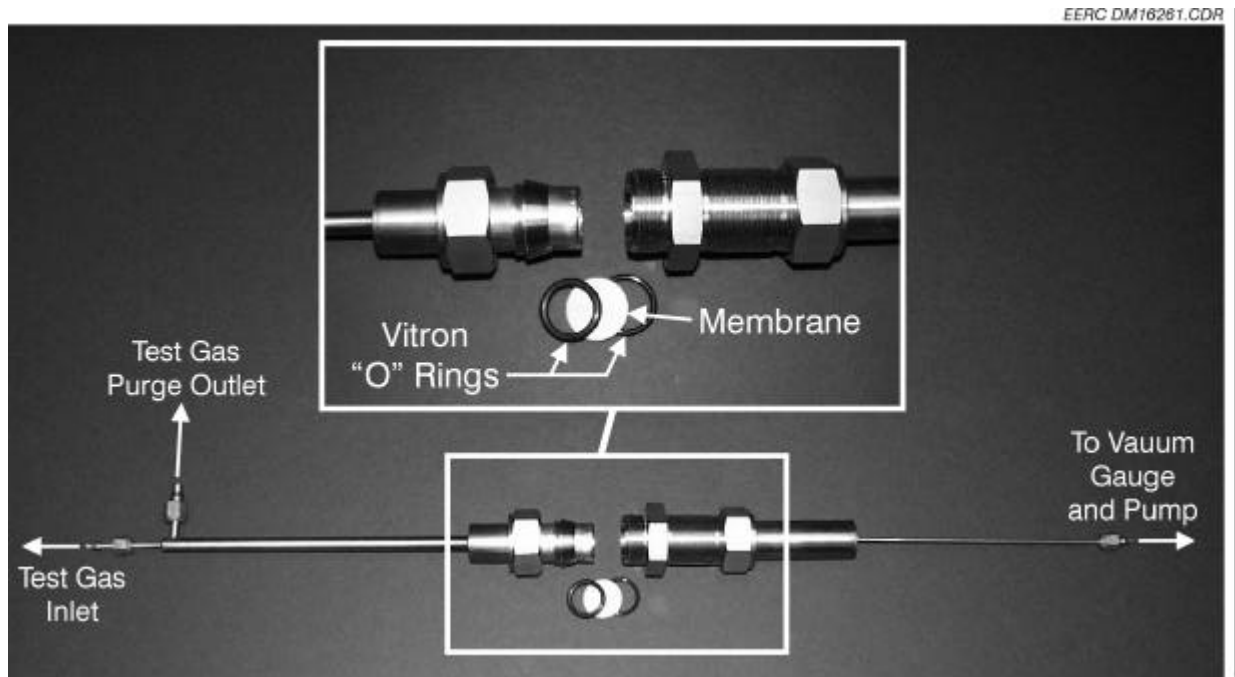


Figure 1. Schematic of the permeation test apparatus.

stainless steel construction permits operation at elevated temperature inside a small tube furnace. Two of the test devices were built to accommodate membranes of 0.75" and 1" diameter.

Once a membrane is installed in the test apparatus, the permeation test is conducted by first purging the inlet side with the test gas (nitrogen or hydrogen) and a vacuum pulled on the outlet side producing a differential pressure across the membrane. The inlet and outlet sides are then isolated from the vacuum and the outlet vacuum gauge monitored. The rate of decay in vacuum is indicative of permeation across the membrane under test. Stainless steel blank "slugs" are used to ensure an impervious barrier for leak testing. Although a manometer would be used for vacuum measurements to quantify permeation rates, a simple vacuum gauge proved suitable for these tests, as either the membranes proved to be either extremely porous to nitrogen flow or effectively impervious to both nitrogen and hydrogen.

Permeation tests were conducted using the 13-mm-diameter 0.2-mm-thick ZnS window attached to a steel backing substrate for mechanical strength at both ambient and elevated temperatures of 100°, 200°, 300°, and 400°C with approximately 0.5 atmospheres of differential pressure across the window. The ZnS window proved impermeable to nitrogen gas as expected. However, when tested with hydrogen gas, there was no perceptible decay in differential pressure across the window after 6 hours for all test conditions. The conclusion was that either negligible permeation of hydrogen gas occurred in ZnS or the exceptional thickness of the ZnS window was resulting in extremely low permeation rates. The ZnS windows are quite fragile, and subsequent attempts to reduce the thickness by further grinding resulted in breakage.

5.3 Thermogravimetric Experiments

The results of the permeation tests indicated that either no permeation of hydrogen gas was occurring or that permeation was occurring, but the thickness of the monolithic ZnS membrane was resulting in negligible permeation rates. To determine if permeation (or at least absorption of hydrogen with ZnS) was occurring, thermogravimetric tests were conducted with small 50-mg samples of powdered ZnS. The samples were heated in argon and in hydrogen atmospheres at a rate of 10°C/min from ambient to 400°C. These results are shown in Figure 2. The ZnS sample heated in argon shows an essentially flat profile as it is heated. However, the sample heated in hydrogen exhibited a gain in weight of 0.4%–0.5% in the temperature range of 180°–200°C. Further heating above 200°C resulted in a substantial weight loss, presumably due to reaction with hydrogen to Zn metal and the formation of hydrogen sulfide.

A second test was performed to determine the reversibility of hydrogen uptake, heating the ZnS in a hydrogen atmosphere to 175°C and remaining at that temperature until hydrogen uptake was complete, and then lowering the temperature to ambient. At 175°C, the hydrogen uptake was approximately 1 mole H₂/mole ZnS. No hydrogen was reevolved from the ZnS in a hydrogen atmosphere, but approximately half the weight uptake was reevolved when the atmosphere was changed to argon at ambient temperature. Subsequent reheating of the same sample in a hydrogen atmosphere resulted in no additional hydrogen uptake. The results of this test are shown in Figure 3. Differential scanning calorimetry of ZnS heated in a hydrogen atmosphere shown in Figure 4 suggests that the uptake of hydrogen is probably due to the formation of a

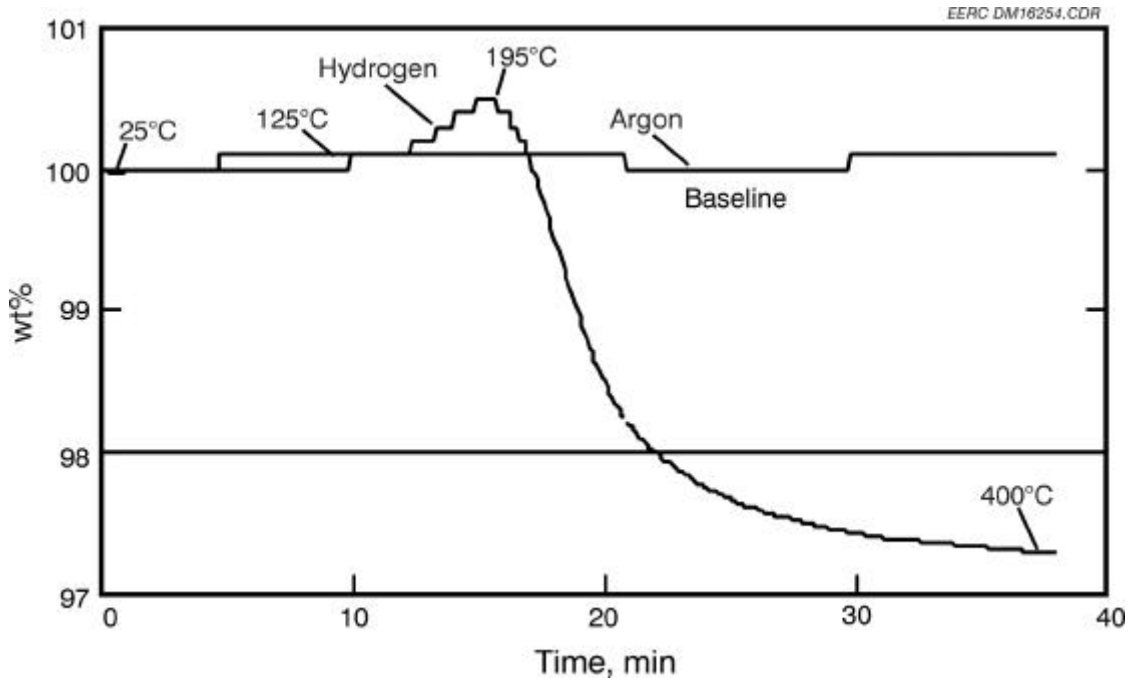


Figure 2. ZnS heated in argon and hydrogen.

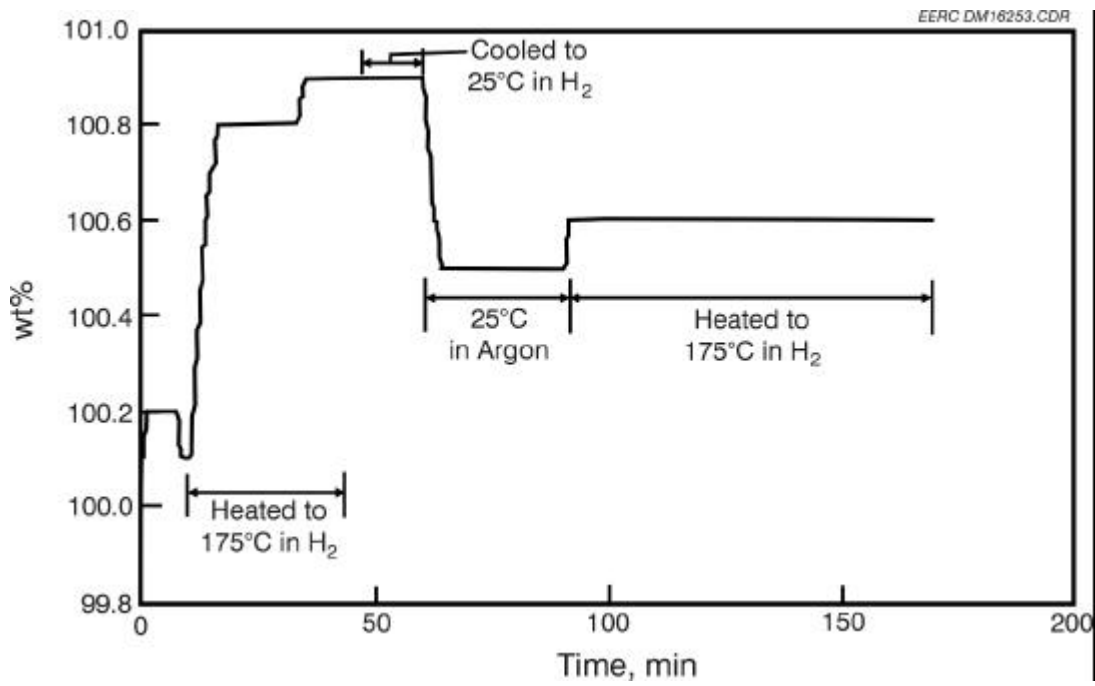


Figure 3. Uptake of hydrogen on ZnS.

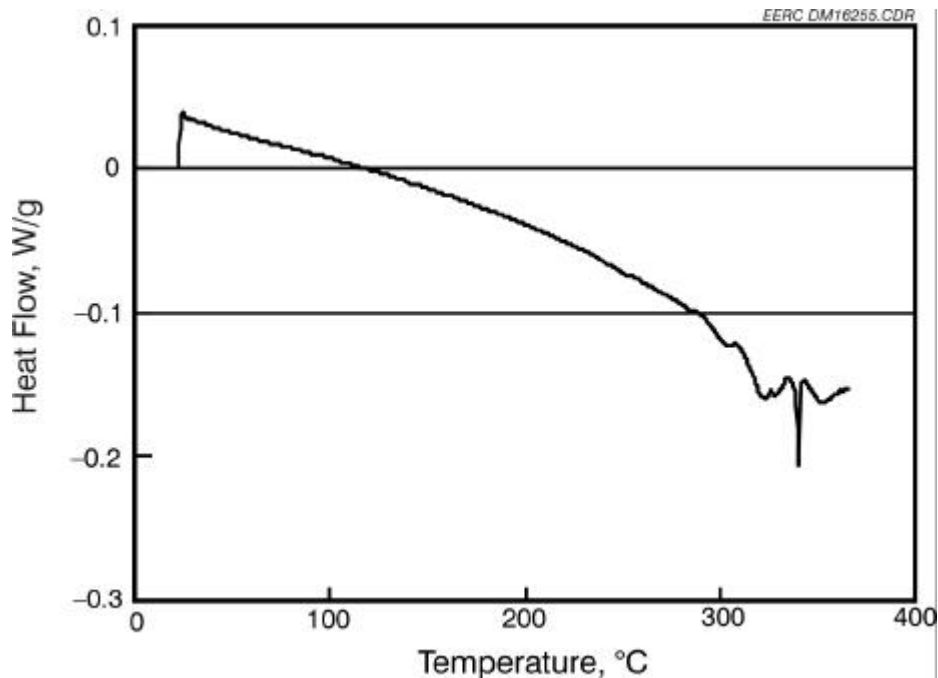


Figure 4. Differential scanning calorimetry of ZnS in hydrogen.

Zn–S–H species resulting in the formation of H_2S . A thermogravimetric test of the analogous ZnO in a hydrogen atmosphere showed a similar initial uptake of hydrogen followed by the decomposition of the oxide. The apparent reduction of the ZnS and ZnO with hydrogen was somewhat surprising at these relatively low temperatures.

6.0 CONCLUSIONS

A likely membrane for future testing of high-temperature hydrogen separation from a gasification product stream was targeted as an inorganic analog of a dense-metal membrane, where the hydrogen would dissolve into and diffuse through the membrane structure. An amorphous membrane such as zinc sulfide appeared to be promising. Previously, ZnS film coating tests had been performed using an electron-beam vacuum coating instrument, with zinc films successfully applied to glass substrates. The coatings appeared relatively stable in air and in a simple simulated gasification atmosphere at elevated temperature.

Because the electron-beam coating instrument suffered irreparable breakdown, several alternative methods were tested in an effort to produce a nitrogen-impermeable, hydrogen-permeable membrane on porous sintered steel substrates. None of the preparation methods proved successful in sealing the porous substrate against nitrogen gas. To provide a nitrogen-impermeable ZnS material to test for hydrogen permeability, two ZnS infrared sample windows were purchased. These relatively thick "membranes" did not show measurable permeation of

hydrogen, either due to lack of absorption or a negligible permeation rate due to their thickness.

To determine if hydrogen was indeed adsorbed, thermogravimetric and differential thermal analyses tests were performed on samples of ZnS powder. A significant uptake of hydrogen gas occurred, corresponding to a maximum of 1 mole H₂ per 1 mole ZnS at a temperature of 175°C. The hydrogen remained in the material at ambient temperature in a hydrogen atmosphere, but approximately 50% would be removed in argon. Reheating in a hydrogen atmosphere resulted in no additional hydrogen uptake. Differential scanning calorimetry indicated that the hydrogen uptake was probably due to the formation of a zinc–sulfur–hydrogen species resulting in the formation of hydrogen sulfide. The zinc sulfide was found to be unstable above approximately 200°C, probably with the reduction to metallic zinc with the evolution of hydrogen sulfide.

The work has shown that ZnS is not a viable candidate for a high-temperature hydrogen separation membrane.

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