SAND2008-3621P
SAND Number: #########

QUARTERLY PROGRESS REPORT

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Project Title: SNL Hydrogen Production & Delivery Program

Covering Period: January 1, 2008 through March 31, 2008

Date of Report: April 30, 2008

Recipient: Sandia National Laboratories

Contact(s): Jay Keller, (925) 294-3316
jokelle@sandia.gov

TABLE OF CONTENTS

Quarterly Progress Report

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Project Title: Task #2 Ultra-thin Proton Conducting Membranes for H_2 Stream Purification with Protective Getter Coatings

Project Period: Q2 FY08 (Jan. 1, 2008 to March 31, 2008)
Date of Report: April 7th, 2008

Principle Investigator: Margaret Welk, 505-284-9630, mewelk@sandia.gov
Other Key National Lab Researchers: Robert Grubbs, Andrea Ambrosini

Sub-Contractors Funded through AOP Task: None

Industrial Partners: None

DOE Managers: Arlene Anderson, DOE Technology Development Manager
Rick Balthaser, DOE Field Project Officer

Project Objective: This project will synthesize ultra thin dense ceramic membranes on microporous supports to separate H_2 with high purity and at a high flux rate. Sulfur getter technology will be incorporated into the mesoporous support layer to address impurities in the feedstock.

Background: This project addresses the separation of high purity H_2 (>99%) from various feed streams using supported thin proton conducting oxide membranes, such as $BaCeO_3$ and $SrTiO_3$.[1,2] These dense oxide membranes exhibit 100% selectivity, resulting in extremely high purity H_2. Sulfur impurities that are typical of many feedstocks will be addressed through the deposition of a getter material, such as ZnO, onto the support structure. Both the getter and the proton conducting materials are deposited in this project using atomic layer deposition (ALD) and plasma-assisted ALD thin film methodologies, which are capable of producing layers on the atomic scale in thickness.

We have demonstrated a low-pressure chemical vapor deposition process, ALD, which is capable of conformal coating of very high aspect ratio structures.[3] Efficient vapor transport at low pressure, combined with selective surface chemistry and sequential introduction of reagents, ensures highly conformal coating and precise thickness control of structures with aspect ratios $>10^3$. For example, we have utilized an ALD process for deposition of ZnO using sequential reactions of diethyl zinc (DEZ) and water at 200°C. Preliminary results indicate formation of a 30 – 40 nm thick film of ZnO formed on the interior surfaces of an alumina support disk, approx. 25 μm below the surface of the disk. Further optimization of exposure and purge times in the ALD reactor have allowed us to uniformly coat all interior surfaces of the support throughout its thickness.

[1] Shimura, T.; Fujimoto, S.; Iwahara, H. Solid State Ionics 143 (2001) 117.
[2] Alberti, G.; Casciola, M. Solid State Ionics 145 (2001) 3.
[3] Mayer, et al, Appl. Phys. Lett. 82, (2003) 2883.

As thinner membranes have higher fluxes, this study is systematically synthesizing and testing membranes over a range of thicknesses. The effective pore sizes of the support material affect the minimum thickness of the membrane; i.e. support materials with smaller pore sizes can support thinner membranes. The support layer will be grown on the support via hydrothermal synthesis and/or sol-gel film synthesis, leveraging the work done at Sandia National Laboratories on microporous membranes under the DOE-EERE. The sulfur getter material, ZnO, will be deposited in a conformal layer on the mesoporous support. This composite design, combining the best characteristics of dense membranes with those of microporous membranes, will exhibit high selectivity owing to gas separation via proton conduction and high flux owing to the thinness of the membrane.

Bringing the high thermal stability (to 800°C), chemical stability, and high selectivity inherent to these proton conductors to a thin (<200 nm) membrane platform will increase the H_2 flux. The resulting membrane-support module will not only produce high purity H_2, but will be durable, withstand significant pressure drops, and can recover a high percentage of the H_2 from the feed stream while being able to withstand substantial impurity levels.

Status:
Task 2.1: Synthesis of an Ultra Thin Proton Conducting Membrane through ALD

Previous work led us to focus on the plasma assisted Atomic Layer Deposition of $SrTiO_3$ as our proton conducting oxide material. An oxygen plasma assisted ALD reactor was constructed last quarter for the deposition of complex perovskites. The reactor is a hybrid of a solid precursor delivery system and an oxygen plasma source. Several specialized precursors were obtained for the plasma assisted ALD deposition of $SrTiO_3$, the titanium precursor, $Ti(isopropoxide)_2(THD)_2$, and the solid phase strontium precursor, 2,2,6,6- tetramethyl-3,5 heptanedionato strontium [aka, Sr(THD)]. Plasma assisted ALD, in comparison with ALD, allows us to control the deposition penetration depth of the H_2 conducting membrane into the support. While a small amount of penetration is necessary for adequate adhesion, we also want to keep the H_2 conducting membrane thin to maximize the flux.

Current work has resulted in the successful deposition of 450 Å of TiO_2 on the Al_2O_3 support. Each cycle of Ti(THD) in the presence of the oxygen plasma delivers 1.5 Å of TiO_2 on the support surface; repeated 150 times results in 450 Å of TiO_2. The delivery of the titanium precursor was monitored with a witness wafer on the quartz crystal microbalance (QCM). Post deposition tests on the Auger confirmed the presence of titanium. See Figure 1. The Auger parameter employs the binding energy of the Ti $2p_{3/2}$ photoemission peak. The $L_3M_{2,3}M_{2,3}$ transition results in the multiplet between 362 and 402 eV.

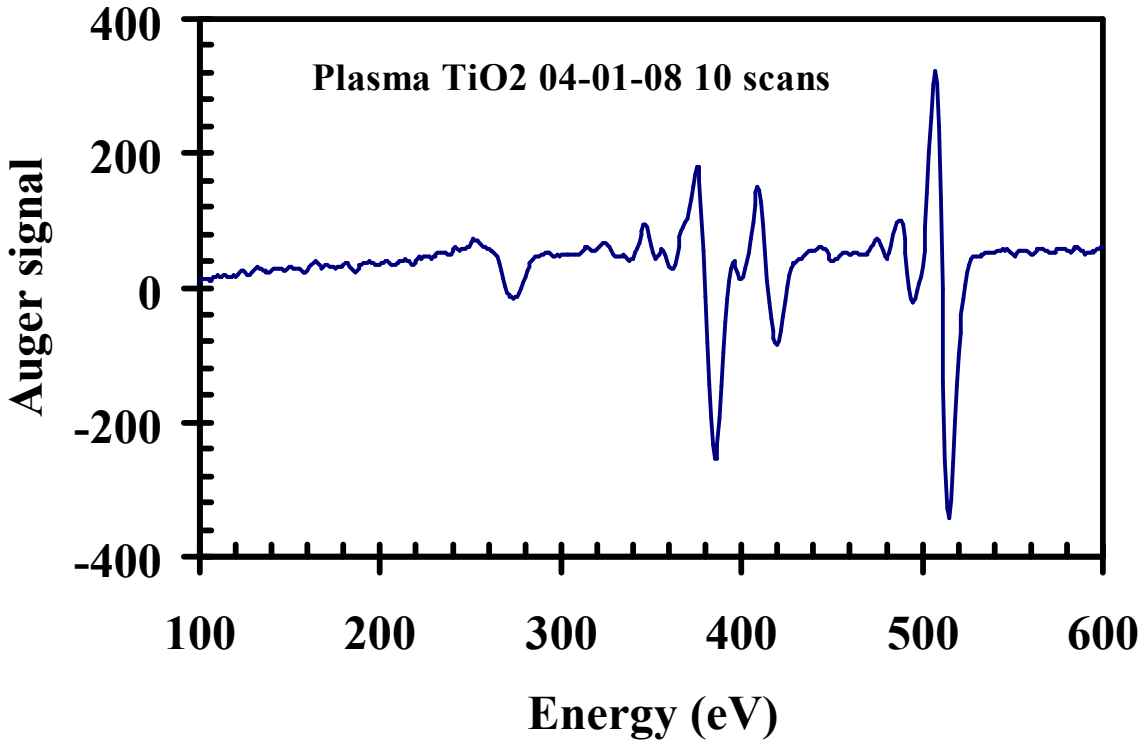

Figure 1. Auger Spectrum of ALD titania

Deposition of the strontium oxide has been more difficult owing to the solid state of the strontium precursor. Modifications to improve the deposition included a study of increasing temperature during precursor delivery and relocation of the sample wafer. Recently, we further modified the sample position in the reactor setup to face perpendicular with respect to the precursor flow. The QCM recorded a mass increase for this set up, and we are progressing to verify the SrO phase currently.

Task 2.2: Synthesis of Mesoporous Silicate Support materials

In order to deposit a layer of proton conducting material thinner than 100 nm, the support surface must have pore openings no larger than 50 nm. As the membrane is a ceramic material, the support we have chosen to work with is an alumina disk or tube with an effective pore size of 1.8 um. We also have alumina supports with an effective pore size of 0.1 um (100nm). To reduce the pore size to 50 nm or less, a mesoporous silicate layer was applied to the porous alumina support.

Using ALD, we have conformally coated the support surface with ZnO in this work, and with Al_2O_3 in other work. A coating of 450Å or 45 nm reduces the effective pore size of the support from 0.1 um to 55nm. Alternatively, last quarter, we were able to use a thixotropic sol to apply a silicate layer to the support that results in pores in the 2-10 nm range.

Our work thus far provides us with supports with pore sizes that bound the range we are interested in: 10 to 50 nm. Before work proceeds down this avenue, research on the compatibility of the perovskite with the silicate coating over the range of temperature cycling is

necessary. Work thus far on the mesoporous support layer is delayed slightly to focus on the deposition of the perovskite, and to further our successful work on the sulfur uptake.

Task 2.3: H_2 permeation

This task is delayed until task 2.1 is on track. Our setup is ready to test membranes when needed.

Task 2.4: Sulfur uptake measurements

Zinc oxide is known to react with H_2S impurities in gas stream to form ZnS, Additionally, ZnO can react with other sulfur impurities, such as SO_2. The capacity, and hence lifetime, of the getter depends on the surface area, thickness, and reactivity of the getter film. Previously, we have demonstrated the ability of the ALD of ZnO reversibly sorb SO_2 and H_2S forming $ZnSO_4$ or ZnS respectively, regenerating ZnO under heating in air. Complete conversion of the ZnO layer was achieved, indicating that the entire mass of the deposited ZnO is available to act as a sulfur getter in this mesoporous structure.

This quarter we began testing the continued reversibility of the sorption ability of the ZnO layer. A ZnO coated Al_2O_3 disk was placed in a furnace, and ramped to 500°C at a ramp rate of 1°C/min. At a flow rate of 1 to 5 ml/min, 2% H_2S in N_2 was passed over the disk for 4 hours, then cooled to room temperature at a rate of 1°C per min. After analysis, the sample was replaced and heated under air for 14 hours and analyzed again. This cycle was repeated 7 times to date. In each instance under H_2S flow, the ZnO layer was completely converted to ZnS, as determined by X-ray diffraction. Complete conversion back to ZnO was achieved each time when heated under air. See Figures 2 and 3.

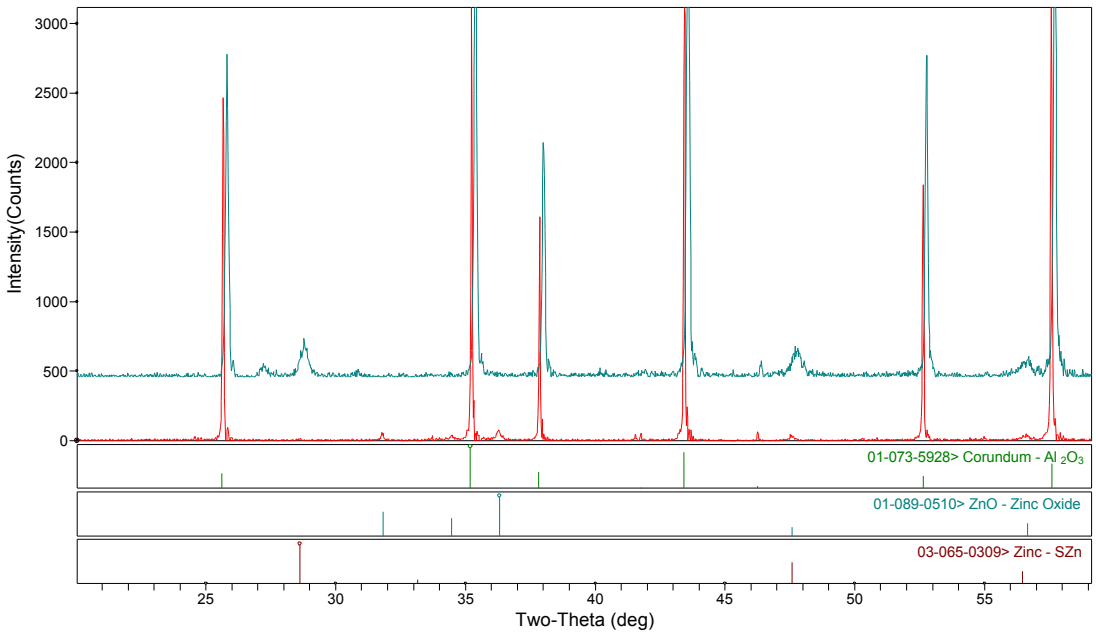

Figure 2. XRD Pattern after one H_2S exposure (blue pattern – ZnS). Red pattern was taken after sample was heated in air (ZnO). Intense peaks are from Al_2O_3 support.

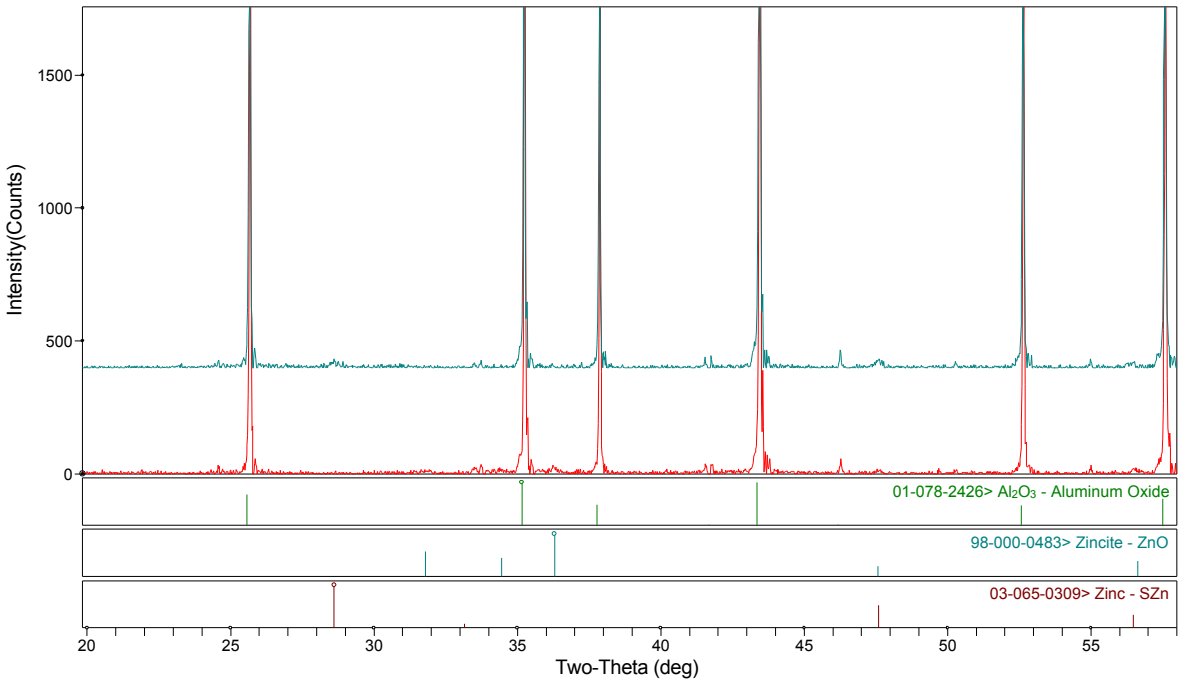

Figure 3. XRD Pattern after 7 cycles. Blue pattern shows ZnS, Red pattern shows ZnO. Intense peaks are from Al_2O_3 support.

Note in the x-ray diffraction patterns the diminution of peak intensity for the desired phase (ZnO or ZnS). We were concerned about decrepitude in the sulfur getter layer resulting in material loss. We performed scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS) to determine whether surface depletion of the zinc phases extended to the interior surfaces of the support. See Figure 4. The EDS reveals that the zinc phases persist after the cycling with no indication of diminution. The distinct band structure visible in these cross section images arises from the fabrication of the alumina support itself; the center of the support is large grained alpha alumina and is coated with small grained gamma alumina to achieve the desired effective pore size.

Task/Milestone Schedule

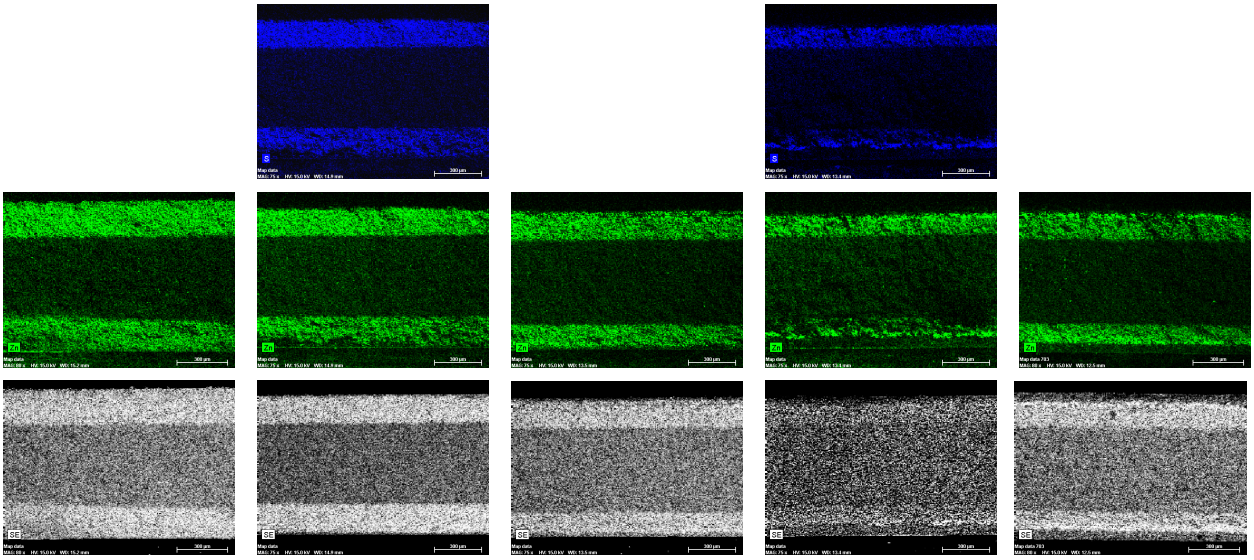

Figure 4. SEM (in black and white) and EDS (in green and blue) scans of coated supports. Areas of green represent the presence of zinc, areas of blue represent areas containing sulfur.

Confident that decrepitude of the zinc coating will not impede our work as it is mitigated by the tortuosity of the support, we are currently moving ahead to quantify the amount of sulfur sorbed and the rate of sorption over the next two quarters. This task is ahead of schedule.

Plans for Next Quarter and Key Issues:
In the next quarter, we will complete the deposition of the proton conducting material on the alumina support using plasma assisted ALD. We will test the proton conduction of the deposited membranes. We will test the compatibility of the silicate mesoporous layer with the deposited perovskites over the temperature range of interest. Further tests on the ZnO coated support as a sulfur getter will be pursued to determine its sulfur sorption capacity.

Patents: none

Publications / Presentations:

M. E. Welk, R. K. Grubbs, A. Ambrosini "Thin Protective Coating of ZnO Using Atomic Layer Deposition" Zing Solid State Chemistry Conference, March 10-13th, 2008.

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Plan	Revised Planned	Actual	Percent Complete	
2.1	Develop ALD synthesis for $SrTiO_3$	01/31/08	05/31/08		85%	Revised to reflect difficulty with SrO deposition.
2.1	Deposit proton conducting films in 4 different thicknesses	06/30/08			0%	Not started.
2.2	Synthesize support films with four different pore sizes	01/31/08	5/31/08		85%	Revised to focus on sulfur uptake.
2.2	Complete studies on effect of pore size and thickness of support layer on membrane thickness.	07/30/08			0%	Not Started
2.3	Test the H_2 permeance of all synthesized membranes	Ongoing			0%	Not Started
2.3	Study effect of H_2 conducting film thickness on permeation	09/30/08			0%	Not Started
2.4	Complete sulfur uptake studies on ZnO	09/30/08			65%	Ahead of Schedule

Quarterly Progress Report

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Project Title: Enabling Hydrogen Embrittlement Modeling of Structural Steels, Task 4

Project Period: Q2, FY08 (January 1, 2008 to March 31, 2008)
Date of Report: April 10, 2008

Principal Investigator: Brian Somerday, 925-294-3141, bpsomer@sandia.gov
Other Key National Lab Researchers: Chris San Marchi (SNL/CA), Kevin Nibur (SNL/CA)

Sub-Contractors Funded through AOP Task: none

Industrial Partners: Petros Sofronis (University of Illinois), David McColskey (NIST)

DOE Managers: Rick Farmer, Hydrogen Production & Delivery Team Lead,
Rick Balthaser, DOE Field Project Officer

Project Objective: The principal objective of this project is to provide an experimental element to the development of models for steel hydrogen gas pipelines. These models include both mechanism-based simulations of hydrogen embrittlement as well as structural integrity methods to predict safety margins for pipelines. The aim of the experimental effort is to establish physical models of hydrogen embrittlement in steels and to generate material properties that serve as model inputs. The focus of the latter is on fracture mechanics properties such as sustained-load cracking thresholds and fatigue crack propagation.

Background: Carbon-manganese steels are candidates for the structural materials in hydrogen gas pipelines, however it is well known that these steels are susceptible to hydrogen embrittlement. While hydrogen embrittlement compromises the structural integrity of steel components, decades of research and industrial experience have allowed many salient variables that affect hydrogen embrittlement of steels to be identified. As a result, there are tangible ideas for managing hydrogen embrittement in steels and quantifying safety margins for steel hydrogen containment structures. For example, fatigue crack propagation aided by hydrogen embrittlement is a key failure mode for steel hydrogen containment structures subjected to pressure cycling. Applying appropriate structural integrity models coupled with measurement of relevant material properties allows quantification of safety margins against fatigue crack growth in hydrogen containment structures.

Status: Efforts during FY08 Q2 focused on several tasks: 1) assessing the performance of the test apparatus for conducting materials testing in high-pressure hydrogen gas under dynamic loading, 2) finalizing the analysis of crack growth kinetics and cracking threshold data for X100 steel over a range of hydrogen gas pressures, and 3) identifying the hydrogen-assisted fracture mode in X100 steel through microscopy analysis.

Significant effort was applied to address challenges associated with the new system for conducting materials testing in high-pressure hydrogen gas under dynamic loading (Figure 1). As indicated in the report from Q1, the principal challenge has been gas leakage around the

sliding seals. These Teflon U-cup sliding seals are intended to minimize frictional forces while containing hydrogen gas at pressures up to 138 MPa. After the pressure vessel was received from the manufacturer, it was determined that gas leak rates past the sliding seals exceeded acceptable levels. As a result, we contacted both the seal manufacturer (OmniSeal) as well as the vessel vendor (Autoclave) to devise a solution to the seal problem. After consultation with both parties, it was concluded that the seals could be redesigned with different materials and a finer surface finish. In addition, the surface finishes of the pull rod and bore in the pressure vessel could also be improved. We agreed on two alternate seal designs with OmniSeal, and both new sets of seals arrived at Sandia at the end of the quarter. Selected pressure vessel components were sent to a local machine shop that specializes in precision surface finishing. The refinished pull rod and bore were also completed at the end of the quarter. The redesigned seals and refinished pressure vessel components will be assembled and leak rates past the seals will be assessed in Q3.

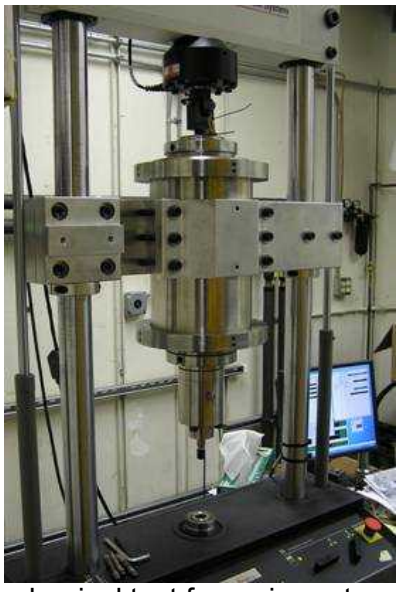

Figure 1. Pressure vessel and mechanical test frame in system for conducting materials tests under dynamic loading in high-pressure hydrogen gas.

Measurements of the sustained-load cracking threshold (K_{TH}) in X100 steel as a function of hydrogen gas pressure were completed. Figure 2 shows the measured K_{TH} *vs* gas pressure trend. Consistent with trends for other steels tested in hydrogen gas, the K_{TH} for X100 decreases as the hydrogen gas pressure increases. Figure 2 shows that K_{TH} was measured at a gas pressure of 21 MPa, which is in the range of gas pressures where hydrogen pipelines could operate. The K_{TH} value at 21 MPa gas pressure (85 MPa-$m^{1/2}$) is a reasonably high value, particularly considering the high strength level of X100 steel. Assuming that an X100 pipeline was constructed with an inner diameter of 30 cm and a wall thickness of 1.3 cm, the pipeline could tolerate an axial defect on the inner surface with a depth equal to 0.6 cm (45% of the wall thickness). A crack of this depth could be easily detected with non-destructive examination techniques.

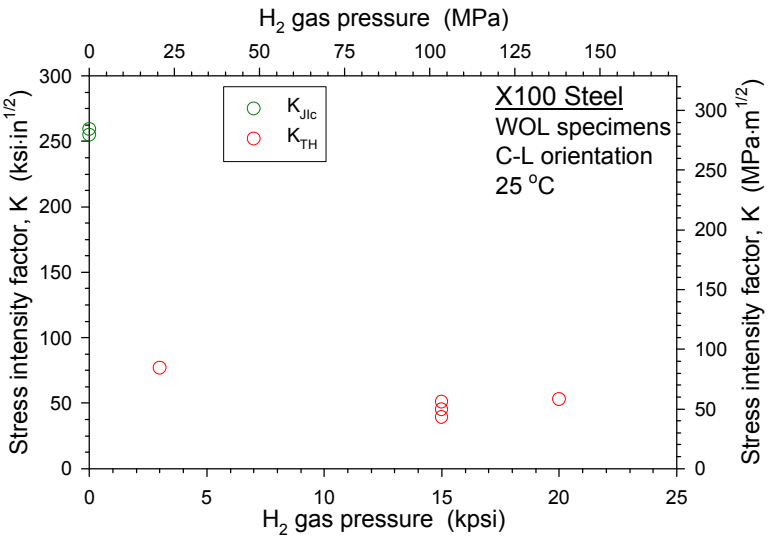

Figure 2. Threshold for sustained-load cracking (K_{TH}) as a function of hydrogen gas pressure for X100 steel.

Microscopy techniques were applied to sustained-load cracking specimens of X100 steel to assess the hydrogen-assisted fracture mode. Figure 3 shows an image of the fracture profile of an X100 specimen tested in 100 MPa hydrogen gas. The image shows the region below the fracture surface, where the crack propagation direction was from right to left. There is clear evidence for the formation of transgranular microcracks in the ferrite phase. This information provides the first step in establishing the detailed hydrogen-assisted fracture mode in X100 steel.

Plans for Next Quarter and Key Issues: Efforts in FY08 Q3 will focus primarily on mitigating gas leakage from the system for testing specimens in high-pressure hydrogen gas under dynamic loading. Once the system is functioning, tensile specimens of X52 and X100 will be tested in 14 MPa hydrogen gas as part of the Pipeline Working Group round robin.

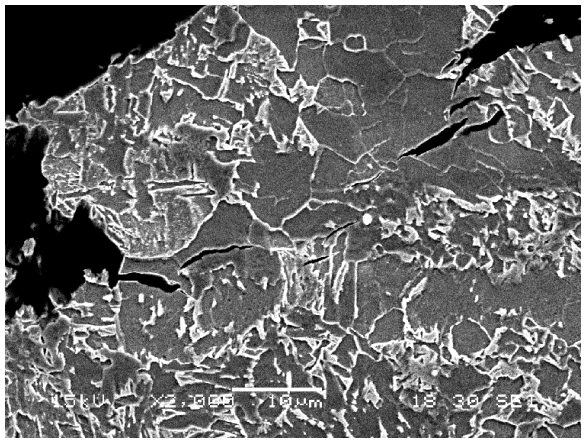

Figure 3. Fracture profile from sustained-load cracking specimen of X100 steel tested in 100 MPa hydrogen gas.

Publications / Presentations:

Task/Milestone Schedule

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Plan	Revised Planned	Actual	Percent Complete	
4.1	Measure cracking kinetics and thresholds of X100 steel under static loading in hydrogen gas pressures from 7 to 70 MPa	01/31/08			100%	
4.1	Measure fatigue crack propagation rates and thresholds of X100 steel in hydrogen gas over the pressure range 7 to 140 MPa	06/30/08			not started	Troubleshooting sliding seals on test equipment

"Hydrogen-Assisted Fracture in Steels for Hydrogen Delivery and Storage", K. Nibur, B. Somerday, C. San Marchi, Materials Innovations in an Emerging Hydrogen Economy, Cocoa Beach, FL, Feb. 2008

"Measurement of Sustained-Load Cracking Thresholds for Steels in Hydrogen Delivery and Storage", K. Nibur, B. Somerday, C. San Marchi, submitted to *2008 Proceedings of the ASME PVP Conference*, 2008

"Structural-Metals Considerations for the Containment of High-Pressure Hydrogen Gas", C. San Marchi, B. Somerday, K. Nibur M. Yip, submitted to *Proceedings of International Symposium on Materials Issues in a Hydrogen Economy*, 2008

Quarterly Progress Report

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Project Title Task 6: Geologic Storage of Hydrogen
Project Period: December 31, 2007to March 31, 2007
Date of Report: April 30, 2008

Principal Investigator: David J. Borns, 505-844-7333, djborns@sandia.gov
Other Key National Lab Researchers: Anna Snider-Lord, 505-284-5588, acsnide@sandia.gov

Sub-Contractors Funded through AOP Task: none

Industrial Partners: none

DOE Managers: Monterey Gardiner, DOE HQ Technology Manager,
Rick Balthaser, DOE Field Project Officer

Project Objective: The expected outcome is to develop a white paper for the DOE hydrogen program. This white paper will cover an understanding of geologic storage, storage types, the advantages and disadvantages of different geologic storage types, a map of locations where storage is available or can be developed in the US. We will develop a section of this paper to analyze the geological, geomechanical, and operational issues of geologic storage, specific to hydrogen.

Background: Geologic storage is used extensively in the oil, natural gas, and compressed air energy industries. To understand the scale of this utilization, 800 million barrels of oil and 100's of billion cubic feet of natural gas are stored geologically in the US. The basic drive for geological storage is that the cost per volume-stored is 3 to 5 times less than surface storage. With this relatively inexpensive way to store large volumes, storage can be situated to buffer seasonal demands, provide continuity in case of disruption in the supply chain, and control congestion in the pipeline system. For example, industry analysis estimates that the current natural gas storage in the US reduces the need for pipelines by 50%.

Geologic cavern storage of hydrogen for industrial use already exists at several locations in Texas. In addition, an evolving hydrogen economy and infrastructure raises similar needs as the natural gas and oil infrastructures. Analyses of the hydrogen infrastructure (Ogden, Williams, Simbeck and Chang, Lord) indicate that there may be an important role for geologic storage. This need, similar to fossil energy stocks, is to buffer seasonal demands, provide continuity in case of disruption in the supply chain, and control congestion in the pipeline system.

Status: Funding for this task was received on May 1, 2007. The task milestones were modified to occur at the time sequence but using May 1, 2007 as a starting date.

Sub-Task 6.1: Overview of Geologic Storage is essentially complete. This subtask covers an understanding of geologic storage, storage types, the advantages and disadvantages of

different geologic storage types. A draft letter report was completed by Anna Snider Lord on 08/31/2007.

Sub-Task 6.2: Develop a Map of Available Geologic Storage in the US is underway. This subtask will produce a map of locations where storage is available or can be developed in the US. Anna Snider-Lord has drafted preliminary maps. Drafts of these maps were forwarded to Monterey Gardiner on 11/19/2007

Subtask 6.3: Analysis of Issues Related to Geologic Storage, Specific to Hydrogen. In the fourth quarter, we held in December 2007 an internal workshop on the issues related to underground storage of hydrogen amongst geomechanics, thermal-mechanical response, fluid dynamics and chemical process subject matter experts. Part of this discussion is the difference in migration process between hydrogen and natural gas. For reservoir storage, hydrogen and natural gas storage may note be analogous. Other issues that were outlined were impacts natural contaminants such as formation gas influx. An action plan was developed for the next quarter. An analytic study of the effects of hydrogen fingering within a porous formation has already been completed. An overview of the project results to date was [presented to the Hydrogen Delivery Tech Team on February 12, 2008. The key project research Anna Snider-Lord returned from Maternity leave.

Plans for Next Quarter and Key Issues:

- The project will focus on the information needs of the ANL "Well to Wheels" Modeling Team for the storage components of the model. The dialog started at the Hydrogen Delivery Tech Team on February 12, 2008
- Sub-Task 6.3: In the coming quarter will complete the work on this task. The goal is a letter report entitled "Analysis of Issues Related to Geologic Storage, Specific to Hydrogen." Initial discussions have started with our staff economic modeler on how Anna Snider-Lord will format the information for ANL.

Patents: none

Publications / Presentations: . An overview of the project results to date was [presented to the Hydrogen Delivery Tech Team on February 12, 2008.

Task/Milestone Schedule **Task 6: Geologic Storage of Hydrogen**

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Plan	Revised Planned	Actual	Percent Complete	
6	6.1. Overview of Geologic Storage (Letter Report on Geologic Storage Overview as applied to Hydrogen)	3/30/2007	08/31/2007		97%	Funding received 5/1/2007
6	6.2. Develop Map of Available Geologic Storage in the US (Letter Report on Map of Available US Storage)	5/30/2007	11/15/2007	11/19/2007	100%	Finalizing map
6	6.3. Analysis of Issues Related to Geologic Storage, Specific to Hydrogen Letter Report on (Issues Related to Geologic Storage)	7/30/2007	1/5/2008		90%	Completing individual analysis of initial issues; e.g., hydrogen fingering; impurity influx
6	Complete White Paper as draft SAND Report for DOE approval and review	9/05/2007	4/15/2008		0%	Not started.