IV.B.3 Investigation of Metal and Chemical Hydrides for Hydrogen Storage in Novel Fuel Cell Systems

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Project Start Date: March 1, 2015
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Develop a methodology that incorporates engineering modeling and analysis tools to screen and down-select storage materials and material systems against cost and performance targets (initially developed and applied by SRNL to light-duty vehicle in the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- Apply this methodology to an initial system design for an Unmanned Underwater Vehicle (UUV) application for the Navy to reduce design time and lead to a more cost effective and better performing final product.
- Maintain hydrogen storage system capabilities and expertise at DOE and SRNL to support a variety of hydrogen and energy initiatives.
- Extends the long-term partnership between DOE and the Department of Defense in hydrogen and renewable energy systems.

Fiscal Year (FY) 2016 Objectives

DOE Funded Activities

- Use engineering analyses to screen hydrogen storage systems against DOD targets & requirements (FY 2015).
- Identify suitable hydrogen storage materials and suitable vehicle demonstration platforms.
- Develop a preliminary design of an integrated UUV design with a solid hydrogen storage system.
- Complete detailed design of a hydrogen storage system.
- Complete integrated system design.

Navy Funded Activities

- Design and build a small bench-scale, alane-based, hydrogen storage vessel.
- Perform preliminary testing on the bench-scale, storage system.
- Package and ship bench-scale vessel and alane material to the Navy.
- Provide technical support to Navy's Naval Underwater Warfare Center (NUWC) for further testing and evaluation.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(D) Durability/Operability

(E) Charging/Discharging Rates

(G) Materials of Construction

(H) Balance of Plant (BOP) Components

(J) Thermal Management

(K) System Life-Cycle Assessment

Technical Targets

SRNL has worked with the Navy to modify the DOE hydrogen storage targets [1] developed for light-duty vehicles to Navy UUV requirements. The proposed hydrogen storage and performance targets for Navy UUV systems include both near-term (Generation 1) and longer-term (Generation 2) requirements. The main difference between near and long-term UUV targets are higher hydrogen storage densities and capacities and higher associated fuel cell average and peak power requirements. While many of the proposed Navy UUV targets are similar to DOE hydrogen storage targets some areas where they differ substantially are in initial material

cost and material durability since most DOD applications can withstand higher costs and shorter operating lifetimes than consumer passenger vehicles.

FY 2016 Accomplishments

- Completed an engineering analysis to screen the most attractive solid-state hydrogen storage materials for UUV applications.
- Alane was selected as the most attractive candidate.
- Testing was performed to demonstrate alane hydrogen storage and delivery performance including steady-state and transient operations.
- Delivered alane material and test module to NUWC for further testing by the Navy.
- Ongoing systems and detailed modeling for UUV platforms are in progress.
- Preliminary analyses indicate two to three times the energy storage compared to battery systems.
- End of year objective is to develop a preliminary prototype alane-based UUV system design and system model for potential Navy applications.
- Long-term path forward is to work with the Navy to develop a final design, fabrication and testing of a prototype UUV system.

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INTRODUCTION

This project builds upon the core capabilities of DOE and SRNL and leverages their collective experiences to new roles in other hydrogen applications, which includes the rapidly growing fuel cell areas for portable power and material handling equipment. This project can provide the basis for additional collaborations between DOE and DOD in fuel cell technology. Advances today in small and portable electronic devices offer consumers more and more options but require more and more power to operate. Today's, and even tomorrow's, batteries are not expected to be able to meet this growing power and capacity demand. This demand is perhaps even more evident in military power systems for soldier as well as unmanned aerial vehicle and UUV applications.

One solution that is actively being evaluated is to use fuel cells. Fuel cells offer efficient and high quality power but require safe, efficient, and cost-effective hydrogen storage systems to make them practical. An attractive means for storing hydrogen is the use of solid-state materials that have demonstrated the ability to increase the density of hydrogen by a factor of more than twice that of liquid hydrogen and more than five times that of compressed gas at 70 MPa [2]. A number of materials exist that appear to be suitable for hydrogen storage for DOD UUV applications. However, the viability of storage systems based on these materials has not been fully established for UUV operating conditions.

APPROACH

The overall approach of this research is to develop a methodology that incorporates engineering modeling and analyses to efficiently screen, design, and select storage materials and material systems against cost and performance targets leading to an initial system design for a UUV application. This methodology, which was initially developed by SRNL and applied to light-duty vehicle in HSECoE, requires updates and modifications for it to be useful for other hydrogen and fuel cell applications. More specifically in this research, this methodology will be applied to UUVs to reduce design time and lead to a more cost effective and better performing final product. The modeling analysis, applied to this project, integrates various hydrogen storage system options with other system components, including fuel cell and balance of plant models to evaluate and compare the overall performance of the onboard hydrogen storage system.

RESULTS

Initial engineering screening analyses on a variety of metal and chemical hydride candidate materials were performed using a modified version of the acceptability envelope tool [3] developed for light-duty vehicles in the HSECoE. The acceptability envelope tool was used to apply the Navy's UUV targets and requirements to several standard hydrogen storage system designs and configurations. Based on the results from the study and discussions with Navy personnel, aluminum hydride or alane (AlH_3) was selected as the leading candidate material. Figures 1a and 1b shows the results from a sensitivity analysis depicting the expected storage performance of an alane-based system against the Navy UUV gravimetric and volumetric hydrogen requirements and a variety of key storage parameters. From Figures 1a and 1b, it can be seen that an alane system can meet or exceed most the longer-term (Generation 2), higher capacity and density UUV targets requested by the Navy.

Following selection of alane as the preliminary candidate hydrogen storage material for this project, a demonstration reactor was designed and fabricated utilizing commercially available parts and connectors. The purpose of the reactor was to provide the Navy with a simple system to evaluate the characteristics of an alane storage system to better understand its operation and performance under a variety of temperature conditions. Since alane is a chemical hydride and not rechargeable with hydrogen pressure, it's performance needs to be further evaluated by the Navy. The test reactor consists of an alane containing vessel that fits inside of a larger annular vessel that contains a heat transfer

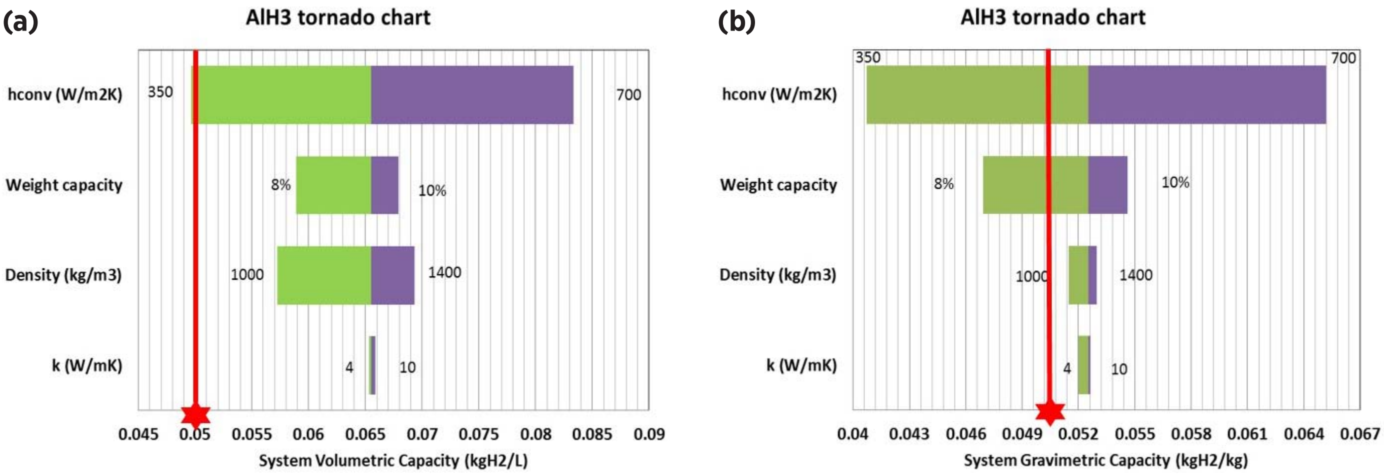
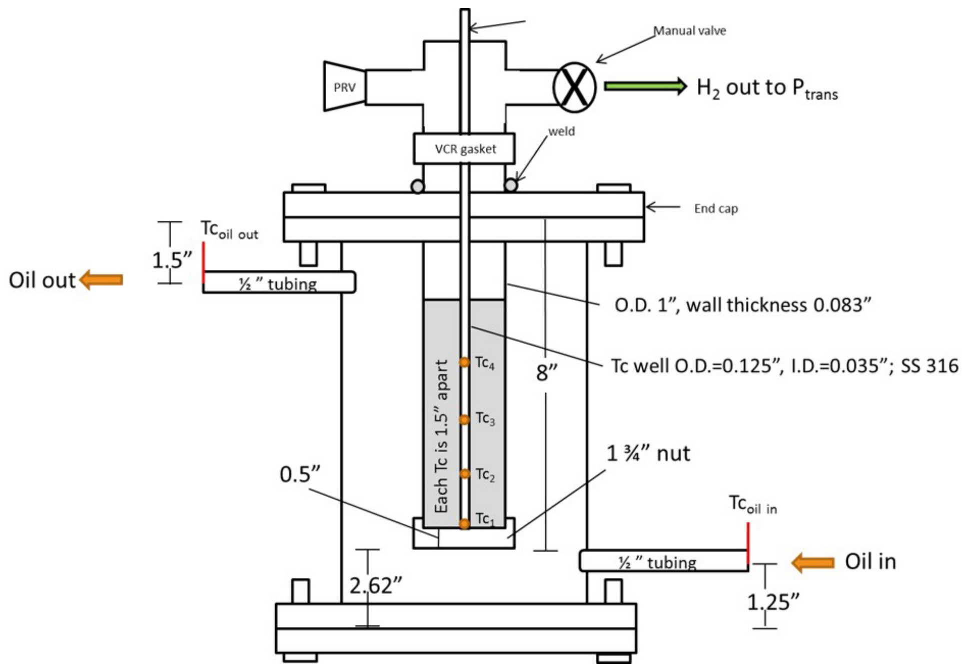


FIGURE 1. Sensitivity analysis results for an alane storage system versus system volumetric density (1a) and gravimetric density (1b)



O.D. – Outside diameter; I.D. - Inside diameter; PRV - Pressure reducing valve

FIGURE 2. Alane test reactor design

fluid (Figure 2). The heat transfer fluid is circulated by two circulator baths. One bath is designated as the hot loop, which is set at a temperature high enough to facilitate hydrogen release from the alane (typically 130–145°C). The other is designated as the cold loop and is set to 20°C. The hot or cold loop is manually directed into the reactor to either initiate the release of hydrogen from alane or to stop the release of hydrogen, respectively. Two large gas collection cylinders (35 L volume) were attached to the test rig for the collection of gas along with a pressure transducer to monitor the rate of hydrogen release from the material. Preliminary test results of the demonstration reactor are shown in Figure 3. The results show the ability to control hydrogen desorption from alane in the system by cooling and heating the reactor. This is a key requirement for the UUV system and further testing of the prototype reactor under various temperature and flow conditions will be carried out by the NUWC.

Models for the UUV alane based hydrogen storage system were developed using Comsol™ Multiphysics software. The models are general and are readily applicable to a wide range of conceptual designs. The model solves the governing equations for mass, momentum, and energy conservation that are coupled to expressions for chemical

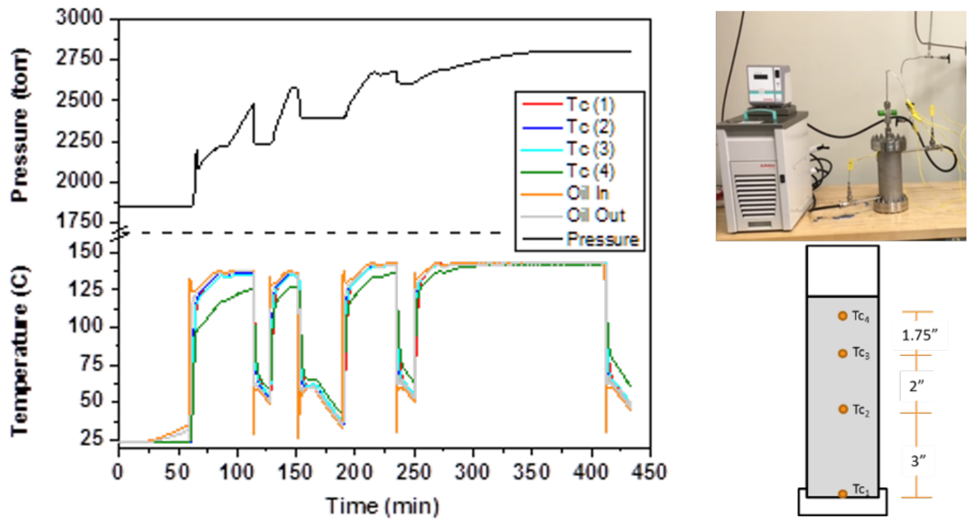


FIGURE 3. Heating and cooling experimental results of test reactor with alane. Inserts shows test reactor connected to oil heating and cooling bath and position of thermocouples during testing.

kinetics and thermodynamics. In this study, the models were applied to the bench-scale demonstration unit.

The test article was modeled in half-symmetry to improve computational speed. The model approximated the alane volume as a cylinder with a radius of 1.06 x 10^{-5} m and a height of 3.1 x 10^{-1} m. The mass and volume of alane are 0.06 kg and 6.81 x 10^{-5} m^3, respectively. The oil flowrate at the inlet was constant at 0.5 m/s. The volume of oil contained in the bath is 1.75 x 10^{-3} m^3. Surrogate alane kinetics and heat of reaction included in the model provided a hydrogen source and a heat sink due to the endothermic nature of the decomposition reaction.

A heating and cooling cycle was modeled as a test calculation to demonstrate the ability to start and stop the release of hydrogen. In this application the system was at an initial temperature of 293.15 K and alane pressure of 1 atm. The oil inlet flowrate was fixed at 0.5 m/s and raised from 293.15 K to 450 K over the first 4 s of the transient, then held at 450 K until 780 s, then reduced to 293.15 K over the next 10 s and held at 293.15 K for the remainder of the calculation. The resulting temperature profiles are shown in Figure 4.

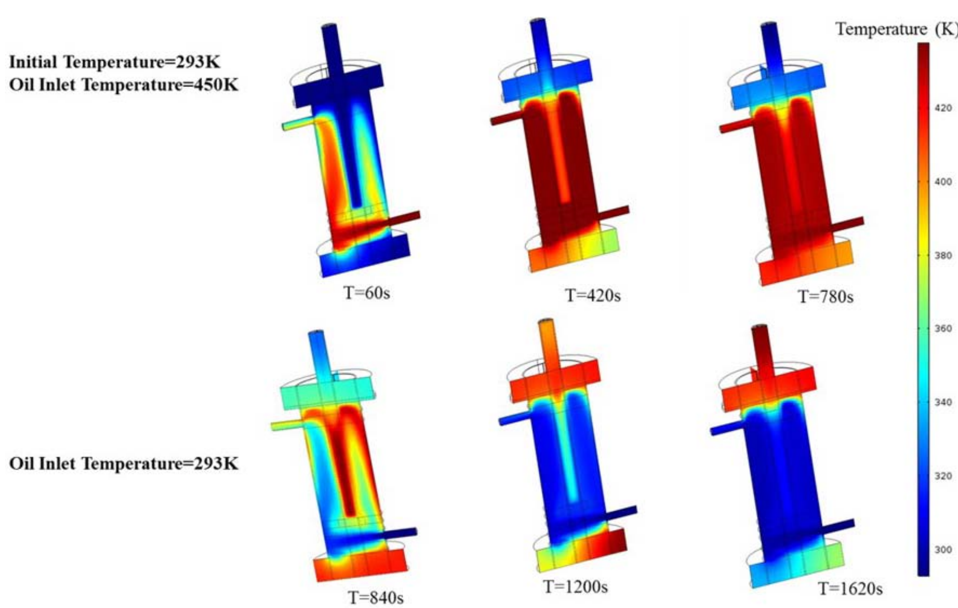


FIGURE 4. Heating and cooling modeling results for test article shipped to Navy

CONCLUSIONS AND FUTURE DIRECTIONS

An engineering analysis was completed to screen the most attractive solid-state hydrogen storage materials for UUV applications. Alane was selected as the most promising candidate material that has the best potential to meet and to exceed many of the Navy UUV targets and requirements. Testing was performed to demonstrate an alane-based hydrogen storage system delivery and performance including steady-state and transient operations. The demonstration reactor was delivered along with a supply of alane material for further testing by the Navy.

Ongoing systems and detailed modeling for UUV platforms are currently underway. Preliminary analyses indicate two to three times the energy storage compared to battery systems. Future objectives include the development of an actual, prototype alane-based UUV system design and system model for potential Navy applications.

2016 PUBLICATIONS/PRESENTATIONS

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