IV.B.2 Investigation of Solid State Hydrides for Autonomous Fuel Cell Vehicles

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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) 2017 Objectives

- Develop a preliminary design of an integrated H_2-fuel cell UUV system design with a solid hydrogen storage system.
- Obtain and generate engineering material property data for alane to be use with prototype system and detailed models.
- Complete detailed design of a hydrogen storage system.
- Design and build a prototype, alane-based, hydrogen storage vessel.
- Perform preliminary testing on the prototype, storage system.
- Package and ship prototype vessel and alane material to the Navy.
- Provide technical support to Navy's Naval Underwater Warfare Center for their 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

(E) Charging/Discharging Rates

(G) Materials of Construction

(H) Balance-of-Plant (BOP) Components

(J) Thermal Management

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 and longer-term 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 Department of Defense applications can withstand higher costs and shorter operating lifetimes than consumer passenger vehicles.

FY 2017 Accomplishments

- Testing was performed to demonstrate alane hydrogen storage properties and delivery performance including steady-state and transient operations.
- Delivered alane material and test module to Naval Underwater Warfare Center for further Navy testing.
- Ongoing systems and detailed modeling for UUV platforms are in progress.
- Key engineering material properties for alane have been generated.
- 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.

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INTRODUCTION

This project builds upon the core capabilities of DOE and SRNL and leverages their collective experiences to support new roles in other hydrogen applications, which includes the rapidly growing fuel cell areas for portable power and material handling equipment. Current battery technology is not able to meet the growing gravimetric and volumetric energy density demand for small portable power 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]. Several materials exist that appear to be suitable for hydrogen storage for Department of Defense UUV applications. However, the viability of storage systems based on these materials for UUV operating conditions has never been demonstrated.

APPROACH

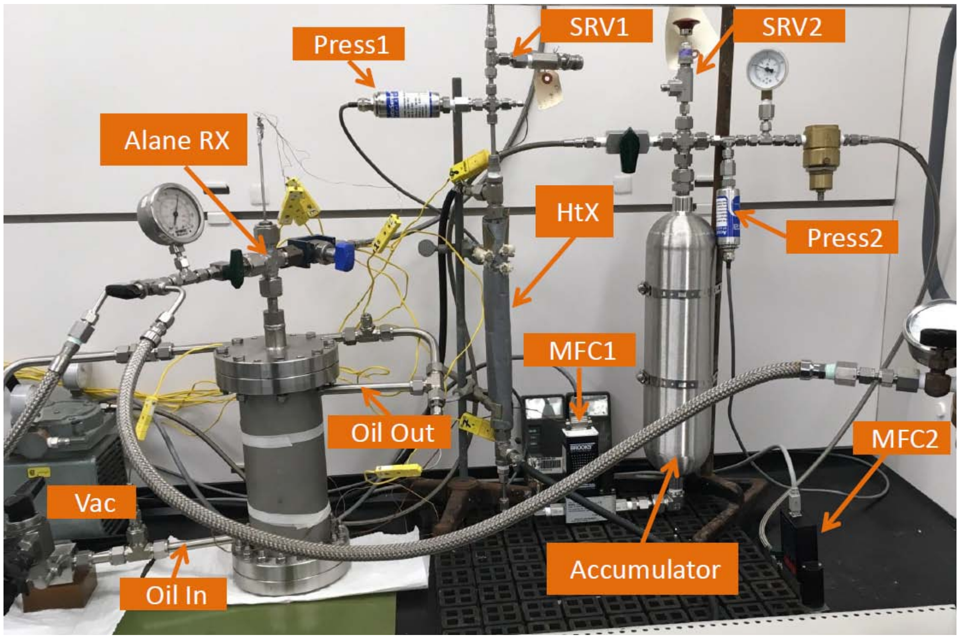
The overall approach of this research is to develop a methodology that incorporates engineering modeling and analyses to efficiently screen, design, and select storage materials and material systems against cost and performance targets leading to an initial system design for a UUV application. This methodology, which was initially developed by SRNL and applied to light-duty vehicles in the 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

Previous year's activities, involved performing an engineering screening analyses on a variety of metal hydrides and chemical hydrogen storage candidate materials 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.

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. Figure 1 shows the SRNL alane reactor (Alane Rx) undergoing testing by the Navy. The tubular reactor is located in an annular shell that provides hot and cold oil to control the discharge of hydrogen from the alane material. Preliminary test results of the demonstration reactor are shown in Figure 2. The results show the ability of the desorbed alane in the system to be controlled by cooling and heating the reactor. This is a key requirement for the UUV system which was verified by the Navy testing.

Engineering material property data was collected for similar alane material that is to be used for future bench and pilot scale studies with the Navy. The data collected included thermal conductivity measurements after various amounts of hydrogen release as shown in Table 1. Results indicate that while the thermal conductivity increases as alane is decomposed into aluminum, additives such as expanded natural graphite (ENG) may be required to enhance the thermal conductivity of the starting alane. Preliminary results from the incorporation of ENG have shown mild improvements of the thermal conductivity at room temperature. Further studies into the degree of volume change during desorption, which will also effect thermal transport, are currently underway. Another key engineering material property measured was desorption and kinetic data. The isothermal desorption of hydrogen from the material was measured between 110–140°C with 1 bar of hydrogen back pressure on the sample initially. The isothermal desorption



MFC – mass flow controller; SRV – safety release valve; RX – reaction vessel; Vac – vacuum pump; HtX – heated transfer fluid line

FIGURE 1. Demonstration alane reactor and testing apparatus

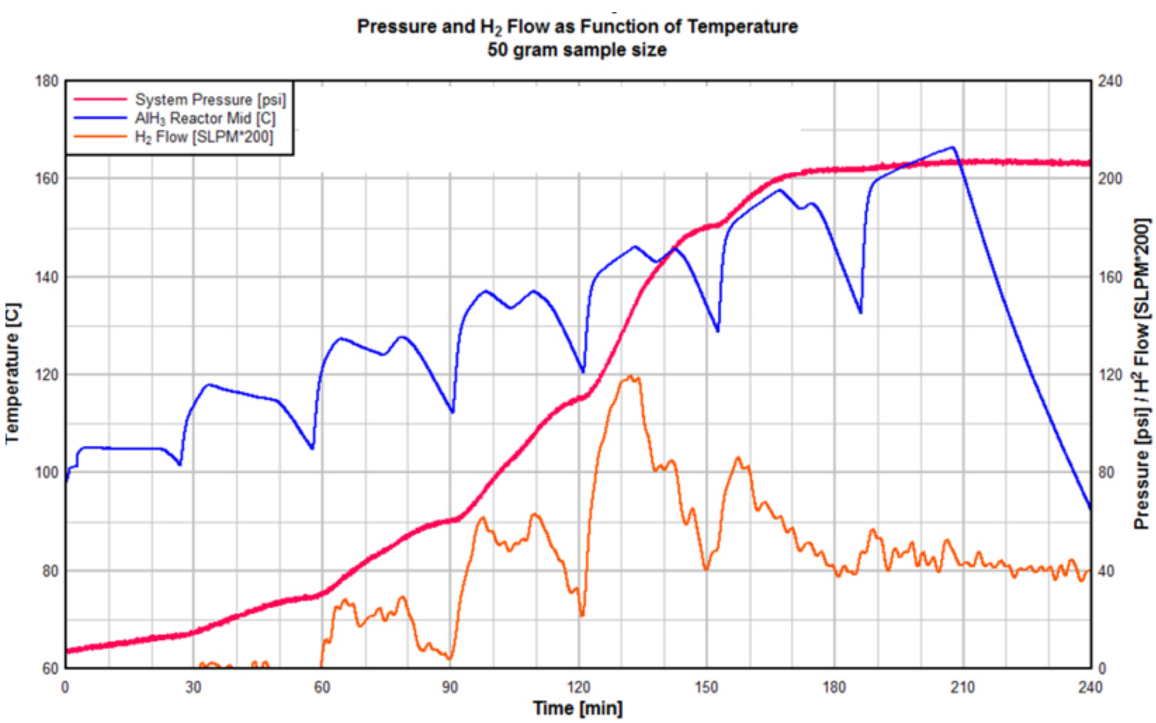


FIGURE 2. Alane decomposition testing and verification results

TABLE 1. Thermal Conductivity of Alane at Various Stages of Decomposition

Sample (wt% ratio)	Thermal Conductivity (W/m*K)
AlH_3:Al (0:100)	18.2
AlH_3:Al (25:75)	13.9
AlH_3:Al (50:50)	9.54
AlH_3:Al (75:25)	5.23
AlH_3:Al (100:0)	0.915

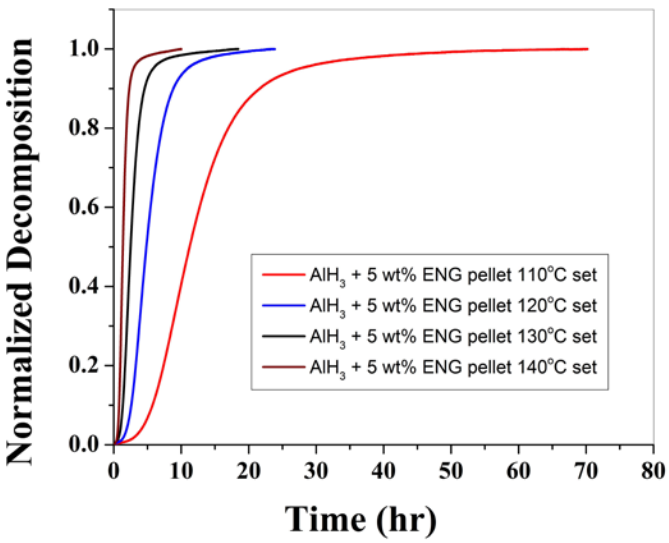


FIGURE 3. Isothermal desorption data from alane with 5 wt% ENG from 110°C to 140°C

plots, shown in Figure 3, demonstrate consistent hydrogen desorption behavior in which the rate of hydrogen release increases as a function of the experiment temperature. The addition of ENG and utilizing a pelletized form of the sample did not have a noticeable effect on the kinetic profiles of hydrogen release.

During the previous year, an alane-based hydrogen storage system model was developed using Comsol™ Multiphysics software. The model was general and was 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 kinetics and thermodynamics. The detailed model was applied to the bench-scale demonstration unit and now is being modified to support the design of the prototype hydrogen storage system for the Navy. As part of this effort, a preliminary high level conceptual design of the alane reactor was performed. This includes the assumptions and restraints described in Tables 2 and 3 for the sizing and heat transfer system in the alane bed and material properties for the alane, respectively.

TABLE 2. Assumptions and Constraints for the Alane Vessel Design

Startup/shut down	10 min
Max diameter	0.254 m
Length	0.229–0.33 m
Thermal power heat transfer fluid	Pressurized water
Inlet/Outlet Temperature	150/130°C
Pressure	10 bar

TABLE 3. Alane Properties

Mass of hydrogen	1.13 kg
Hydrogen flow rate	0.2 g/min for about 96 h
DH, heat of desorption	7.6 kJ/mol H_2
Cp, heat capacity	1340 J/kg K
k. thermal conductivity	7 W/m K
wf, weight fraction	10%
Bulk density	1000 kg/m^3

FIGURE 4. Complete power system design

A high-level model, including mass and energy balance of the reactive system and the heat transfer system, has been developed. A shell and tube heat exchanger concept has been assumed. The cooling power to shut down the reactor in 10 minutes has been included in the preliminary heat exchanger design model. The results from the model indicate that the assumptions and constraints made for the vessel design and alane properties (Tables 2 and 3, respectively) will allow the alane vessel to fit in the designated area allotted inside of the UUV. Figure 4 illustrates the conceptual design of the power system. This model accounts for the space occupied by the shell and tube heat exchanger with additional space to allow for additional balance of plant components.

CONCLUSIONS AND UPCOMING ACTIVITIES

Alane was selected as the most promising candidate material due to the potential to meet and exceed many of the Navy UUV requirements, with the potential to provide twice the energy storage of current battery systems. Navy testing of a SRNL supplied demonstration unit was performed to validate the hydrogen delivery and performance of an alane-based hydrogen storage system. Key engineering and material property data for alane were generated for ongoing prototype model and design efforts. Preliminary modeling activities indicated that alane-based power systems can double the range of current battery-based UUVs. System and detailed modeling for a prototype UUV design are currently underway this fiscal year with plans to fabricate and deliver a prototype storage system to the Navy in early 2018.

2017 PUBLICATIONS/PRESENTATIONS

1. Teprovich J. et al, "ONR Undersea Power and Energy Program Review," Arlington, VA, March 28–30, 2017.

2. Teprovich J. et al., "Investigation of Solid State Hydrides for Autonomous Fuel Cell Vehicles," Annual Merit Review, Washington D.C., June 8, 2017.

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3. Corgnale C, Hardy B.J., Tamburello D.A., Garrison S.L., Anton D.L., Acceptability envelope for metal hydride-based hydrogen storage systems. Int J Hydrogen Energy 2012;37:2812e24 http://dx.doi.org/10.1016/j.ijhydene.2011.07.037.