Investigation of Solid-State Hydrides for Autonomous Fuel Cell Vehicles

Patrick A. Ward (Primary Contact), Ragaiy Zidan, Scott McWhorter, David Tamburello
Savannah River National Laboratory
301 Gateway Dr.
Aiken, SC 29803
Phone: (803) 646-6358
Email: Patrick.Ward@srnl.doe.gov

DOE Manager: Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov

Project Start Date: October 1, 2016
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 Savannah River National Laboratory [SRNL] to light-duty vehicles 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.
- Extend the long-term partnership between DOE and the Department of Defense in hydrogen and renewable energy systems.

Fiscal Year (FY) 2018 Objectives

- Obtain kinetic data describing the hydrogen release from α-alane produced by the newly developed SRNL method.
- Design, construct, and evaluate a prototype alane storage system incorporating enhanced thermal transport strategies and simulated heat transfer fluid capabilities.
- Demonstrate a hydrogen storage heat exchanger system capable of heating the alane storage system to operational temperatures within 10 minutes.
- Provide experimental confirmation that available heat transfer fluid will be sufficient for complete hydrogen removal from the storage bed.
- Evaluate and mitigate any material contraction issues that may occur during hydrogen desorption and reduce thermal contact with heat exchanger surfaces.

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[1]:

- System Weight and Volume
- System Cost
- Efficiency
- Durability
- Charging/Discharging Rates
- Materials of Construction
- Balance-of-Plant (BOP) Components
- Thermal Management.

Technical Targets

SRNL has worked with the Navy to develop hydrogen storage targets for Navy UUV requirements, based initially on the DOE hydrogen storage targets for light-duty vehicles [1]. 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

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

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 because most Department of Defense applications can withstand higher costs and shorter operating lifetimes than consumer passenger vehicles.

FY 2018 Accomplishments

- Designed, constructed, and evaluated a demonstration alane storage system at a scale of 232 g alane produced by the SRNL process intensified method.
- Acquired kinetic data on newly developed alane from the SRNL process.
- Developed enhanced thermal transport strategies for the alane hydrogen storage system.
- Evaluated contraction possibilities in the alane storage bed and determined that no significant contraction was observed.
- Exceeded UUV system startup time target of 10 minutes in shell and tube configuration alane storage bed demonstration vessel.
- Demonstrated that volumetric targets could be met for storage of alane to achieve 2x operational time versus lithium ion batteries.

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 to use solid-state materials that have demonstrated the ability to increase the volumetric density of hydrogen. The volumetric hydrogen density of alane (~140 g/L assuming crystal density) is more than twice that of liquid hydrogen (71 g/L) and more than three times that of compressed gas at 700 bar (40 g/L) [2]. Several materials exist that appear to be suitable for hydrogen storage for Department of Defense UUV applications, which have less stringent targets for material costs and reversibility. 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 research activities performed engineering screening analyses on a variety of metal hydrides and chemical hydrogen storage candidate materials using a modified version of the acceptability envelope tool developed for light-duty vehicles in the HSECoE [3]. Aluminum hydride (alane) was selected as the ideal candidate due to desirable volumetric and gravimetric hydrogen storage capacity and suitable desorption temperatures. Following the material selection, a demonstration reactor was developed to evaluate the release kinetics and operational feasibility of the material. For these experiments, alane from ATK, produced under different and more costly conditions, was utilized. Decomposition kinetics data was collected for ATK alane and a kinetics expression was derived to provide experimental input for system models. Recently SRNL has developed a process intensified method to produce large batch quantities of pure α-alane. This method has gained significant interest and is believed to be the lowest-cost method of alane production demonstrated on a reasonable scale (>200 grams). While the only differences between ATK alane and SRNL alane lie in the particle shape, size, and passivation layer, these differences affect the kinetics of hydrogen desorption and the long-term stability of the material. The effect of α-alane particle size is clearly illustrated by the difference in onset desorption temperatures observed by thermal gravimetric analysis. In order to appropriately evaluate the use of SRNL alane in the UUV system, desorption isotherms were carried out (Figure 1) to provide a kinetics expression for this material.

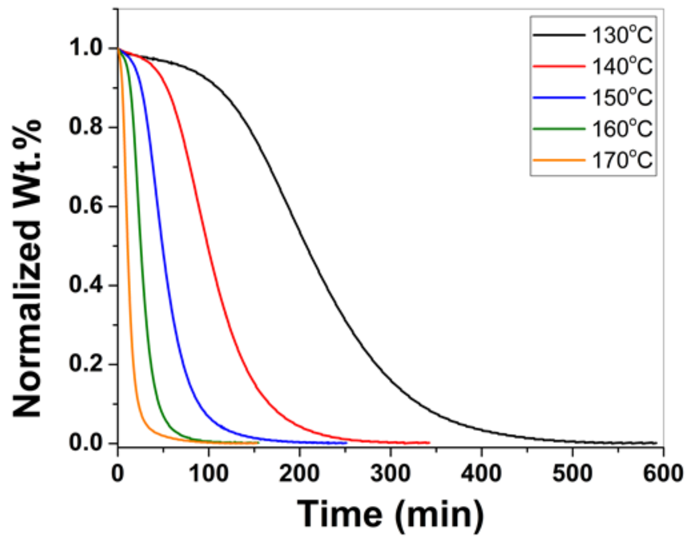
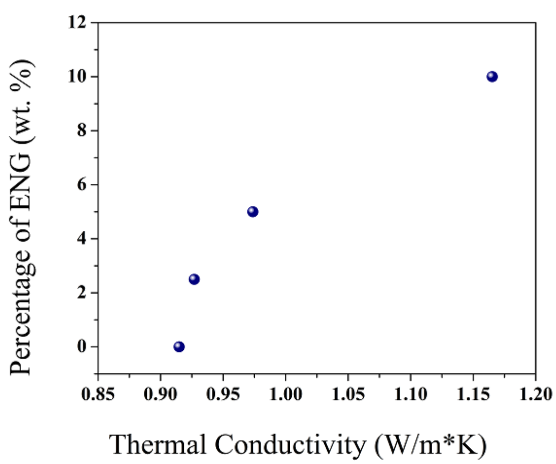


Figure 1. Isothermal desorption curves of α-alane produced by the SRNL method

To simplify the operation and design of the alane storage bed and heat exchanger design, a simple tube and shell design was selected to demonstrate the feasibility of utilizing alane in a UUV. To ensure adequate heat transfer rates within the storage bed, various methods of enhancing thermal transport were explored. It was found that the addition of expanded natural graphite (ENG) not only enhanced the thermal conductivity of the material, as shown in Figure 2, but also assisted in the compression of alane to achieve a higher packing density. Additionally, aluminum foil was used during alane pellet compression to enhance thermal conductivity and structural stability of the pellets. Another critical factor to consider in a metal hydride storage bed is the expansion or contraction of the material during hydrogen uptake and release. Because the equilibrium pressure of alane is far too great for the material to be considered reversible, only the contraction of the material needs to be considered for this application. Material contraction would hinder thermal transport by reducing material contact with the heat exchanger walls. The desorption of various alane pellets demonstrated no measurable change in the dimensions of the pellet after desorption. Although aluminum (decomposition product of alane) is denser than aluminum hydride, the particles tend to retain their initial shape after desorption and are composed of agglomerates of nanoparticles of aluminum as shown in Figure 3.



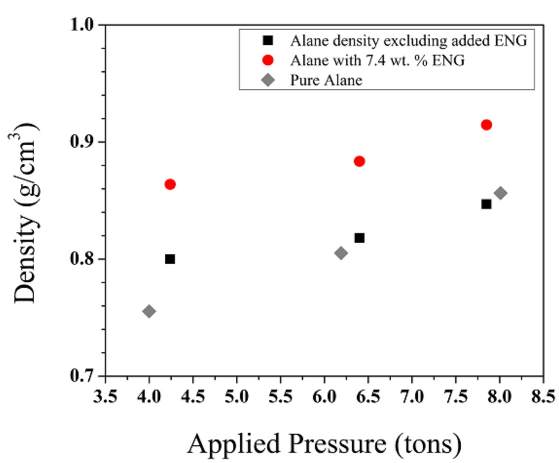


Figure 2. Thermal conductivity of SRNL alane with the addition of ENG at different weight % loadings (left) and density of alane at different applied pressures (right)

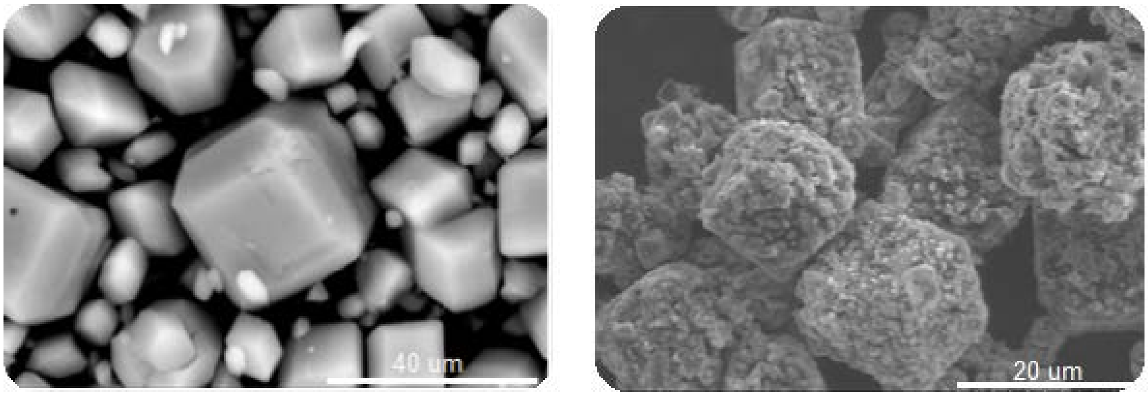


Figure 3. Scanning electron microscopy image of alane before and after desorption

To more accurately demonstrate the feasibility of the alane in the UUV system, a demonstration vessel was constructed that mimics the heat transfer fluid availability, wall thicknesses, and material volume to heat transfer fluid volume ratios that would be found in the UUV system. The demonstration vessel experiments were carried out with 232 g of SRNL alane and demonstrated that the target time of 10 minutes to preheat the storage vessel and alane to the target operational temperatures could easily be exceeded, as shown in Figure 4. These experiments also verified that the amount of heat available to desorb hydrogen from alane was sufficient (although insulation would play a significant role in extended operation). It was also demonstrated that enough alane could be stored in the given volume to extend the operational time of the UUV by a factor of 2, but modifications in the heat exchanger design would be necessary to reduce the system weight to maintain neutral buoyancy and provide adequate pressure ratings for the storage vessel.

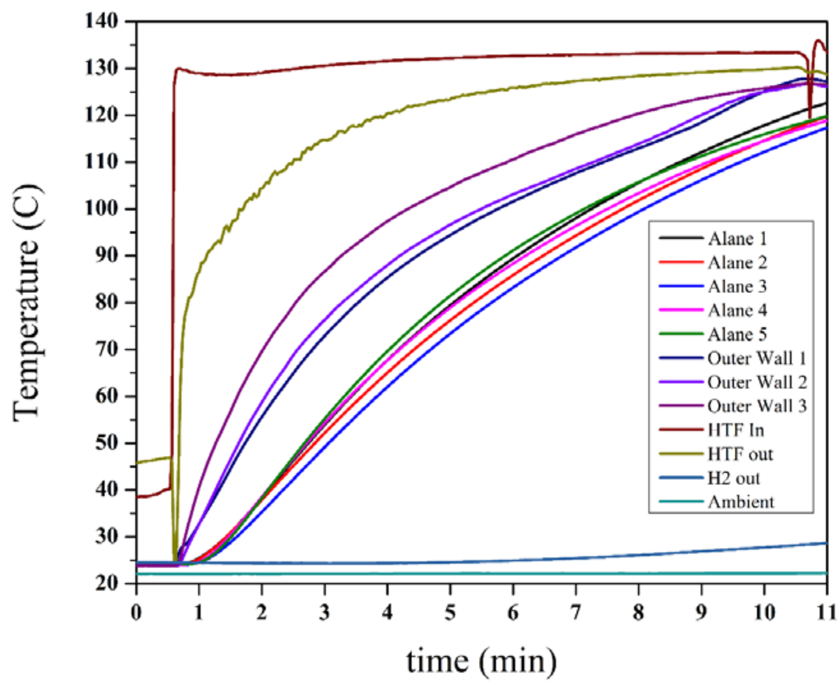


Figure 4. Temperature profile for alane demonstration vessel during initial heating to simulate on-ship preheating

CONCLUSIONS AND UPCOMING ACTIVITIES

While significant progress on the development of a hydrogen storage system for extended operation of UUVs has been accomplished, the cost and commercial availability of alane still prohibits its near-term use in this application. Due to the relatively low hydrogen release temperature of alane and its exceptional volumetric and gravimetric hydrogen capacity, aluminum hydride is still the favorable material for extending the operational time in portable power applications. Full-scale modeling of the hydrogen storage system using experimental data acquired for the alane produced by a process intensified method developed by SRNL is needed to give a higher confidence in overall system performance and provide information for optimizing operational conditions. Additionally, optimization of the heat exchanger design and construction materials needs to be evaluated to achieve system weight targets. Future work will focus on system modeling using experimental data acquired previously and the development of reduced-cost methods to produce alane at an industrial scale.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. R. Zidan and P. Ward. "Mechanochemical Solid/Liquid Reaction in Formation of Alane." Patent Application Number 15/482,913 (issued November 27, 2018).

FY 2018 PUBLICATIONS/PRESENTATIONS

1. P. Ward et al., "Investigation of Solid State Hydrides for Autonomous Fuel Cell Vehicles," Presentation at the DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 13–15, 2018.

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2. L. Klebanoff and J. Keller, "5-Year Review of Metal Hydride Center of Excellence," *Int. J. Hydrogen Energy* 38 (2013) 4533–4576. In *Proceedings of the 2010 U.S. DOE Hydrogen Program Annual Merit Review*, Washington, DC, 7–11 June 2010, https://www.hydrogen.energy.gov/pdfs/review10/st029_klebanoff_2010_o_web.pdf.

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