IV.H.1 NaSi and Na-SG Powder Hydrogen Fuel Cells

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- Trulite Inc., El Dorado Hills, CA
- University of Texas, Austin, TX

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Objectives

- Develop and demonstrate a controllable hydrogen generation system based on sodium silicide powder for portable fuel cell applications.
- Develop specific reaction control mechanisms which encompass water feeding, thermal management, and reaction site maximization.
- Verify operation of all core balance of plant and reaction control components in a laboratory setup.
- Design, fabricate, and assemble a prototype system packaged in a professional manner which generates hydrogen in a controlled manner with minimal user intervention.
- Demonstrate operation with a fuel cell system capable of 250 W.
- Conduct core research to evaluate the potential for ultra-high performance sodium silicide materials.
- Develop the appropriate manufacturing methods to readily scale production of sodium silicide in follow-on activities.

Technical Barriers

This project addresses the following Storage technical barriers of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

(B) System Cost

(J) Thermal Management

Technical Targets

The developed sodium silicide technology is specifically focused on portable power applications such as back-up power, mobile workstations, and emergency responders. The specific target range includes applications from 50 to 500 W. The developed technology is expected to be scalable to at least 1 kW for applications such as lawn mowers (known to be highly polluting) and electric bicycles.

The developed technology will likely not meet all DOE technical targets, but there has been a significant focus on customer attributes such as safe operation, fast starting, rapid restarting, low-pressure operation, and ease of use. While this work addresses many of the technical barrier topic areas as outlined in the Fuel Cell Technologies Program Plan, this work is focused on portable power applications that do not have defined DOE targets.

The current effort seeks to establish system technology using sodium silicide. Not only does sodium silicide enable systems that are low cost and reliable, sodium silicide has a high energy density of 3,267 Wh/kg (lower heating value, LHV). SiGNa anticipates the development of advanced silicides with comparable system control architectures which will further increase performance metrics and are capable of over 4,200 Wh/kg (LHV).

The cost of energy storage for portable power applications is expected to approach DOE targets compared to those for vehicle technologies as it is expected to reach $4.47/kWh. Further cost reductions may be realized through manufacturing scale up and other industrial usage demands of sodium silicide and the waste product, sodium silicate.

Accomplishments

Significant progress has been made in the development hydrogen generation system technology for fuel cell applications. The work in this program includes the following accomplishments:

- Fabricated and tested a laboratory system which demonstrated key performance attributes: 9.8 wt% hydrogen yield on a powder basis, multiple re-starts with up to one week of off time, and controlled generation (~3 slpm) at low pressures (~30 psi).
- Successfully completed bench top testing and sustained operation of a 300 W fuel cell-powered electric bicycle.
- Developed a hydrogen filtration system and verified results with gas chromatography verifying 99.99% hydrogen purity.
- Completed construction of standalone hydrogen generation development unit capable of 4 slpm and a capacity of 1,000 liters of hydrogen.
- Produced (via toll manufacturer) over 25 kg of sodium silicide.
- Demonstrated combined water/powder energy density of 1,600 Wh/kg LHV (1,854 Wh/kg if 50% water recirculation is assumed).

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Introduction

SiGNa Chemistry, Inc. is developing a unique hydrogen storage mechanism utilizing SiGNa's air-stable sodium silicide powder derivatives (e.g. Na_4Si_4). SiGNa's stabilized powders have been shown to produce 9.8 wt% H_2. The primary goal of this work is to develop a prototype system including all balance-of-plant components which controllably generates hydrogen based on usage requirements. SiGNa Chemistry will initially target a 3 slpm (~250 W net output) hydrogen generation system. This flow rate generation can support a wide range of applications such as:

- supplemental hydrogen for diesel trucks for improved fuel efficiency and reduced emissions
- primary power for small vehicles (i.e. scooters, mini-bikes)
- emergency responder stations
- backup power
- surveillance
- other off-grid applications

While numerous hydrogen production chemistries have been explored for portable systems such as sodium borohydride or methanol reforming, commercialization has been limited to high-pressure tanks and metal hydrides - both of which have significant usability issues. SiGNa's newly developed class of sodium silicides such as, Na_4Si_4, rapidly react with water to form hydrogen and a benign, industrially useful, by-product, sodium silicate.

$$2\ NaSi(s) + 5\ H_2O(\ell) \rightarrow 5\ H_2(g) + Na_2Si_2O_5\ (aq)$$

SiGNa has developed system implementation technology to facilitate this reaction in a manner that is highly controllable with high flow capability at low pressures with excellent re-start characteristics.

Approach

The overall approach is summarized in Figure 1. The basic architecture is straightforward; simply add water to powder. Water solutions, such as salt water and water/alcohol mixtures, were also tested and verified to yield a controllable hydrogen flow rate with no impurities (as tested on an Agilent 6850 gas chromatograph). A micro-spray water distribution system has been developed to increase the active reaction area. For a "single-start" reaction, this distribution system is not necessary as the bed will self-mix and fully react large quantities of powder. To rapidly start a cold, partially reacted solution, the micro-spray system sprays water streams on un-reacted powder regions throughout the chamber.

SiGNa first developed a series of clear reaction vessels to visualize the reaction and optimize the parameters. This series of breadboard test vehicles was used to test the various control components and demonstrate core reaction characteristics. The results of these experiments have been incorporated to develop a standalone hydrogen generation system. Basic operation of the hydrogen generation system (Figure 2) has been verified with a Trulite 300 W fuel cell system (Figure 3) and then modified to fuel a hydrogen-fueled electric bicycle (Figure 4). During this project, material production has jumped from a 100 gram laboratory process to a >4 kg batch reactor. SiGNa is currently working with an established toll manufacturer with expertise in alkali metals to continue the scale-up of a next-generation manufacturing process.

Results

Cartridge

A number of reaction vessels have been tested ranging from 30 to 1,200 ml. This work led to the development of a 1.2 liter cartridge fabricated using an impact extrusion process - similar to a paint can - for low-cost production. The cartridges have a quick-connect interface and are used in conjunction with both the Trulite 300 W fuel cell and a 300 W electric bicycle.

Reaction

The water feed and distribution system primarily consists of the pump and a micro-nozzle network. In practice, there are significant challenges in getting a far reaching spray at very low water flow rates (<1 ml/min).

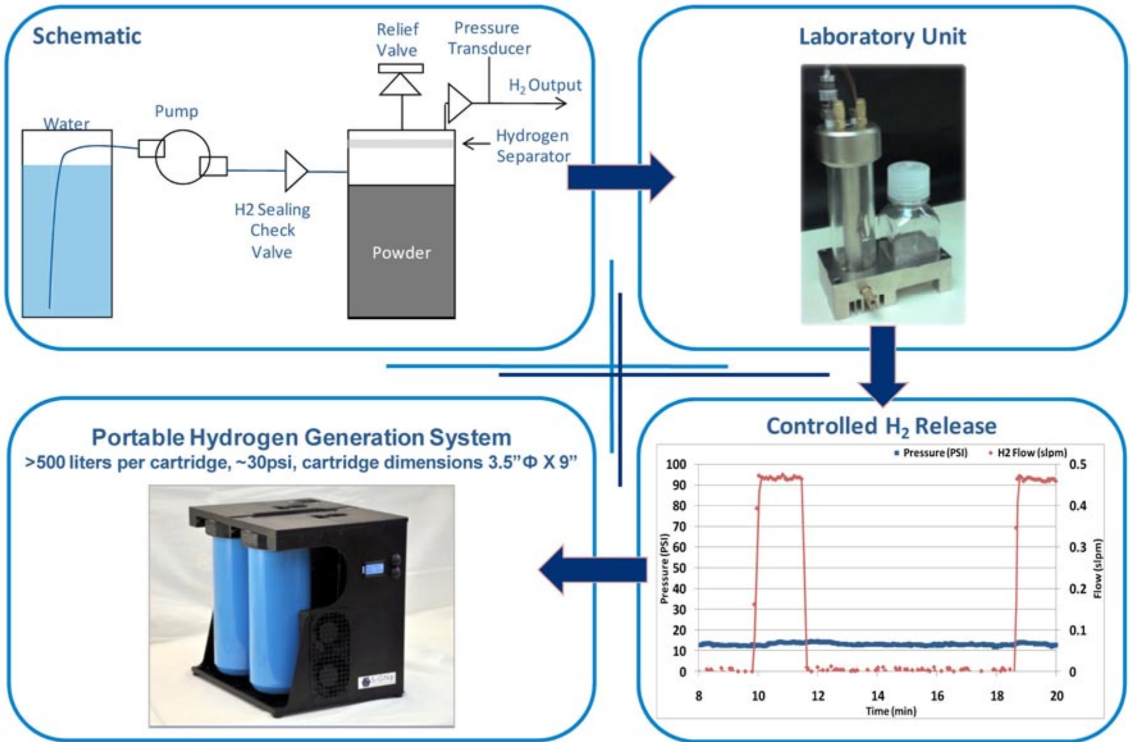

FIGURE 1. Hydrogen Generation Overview

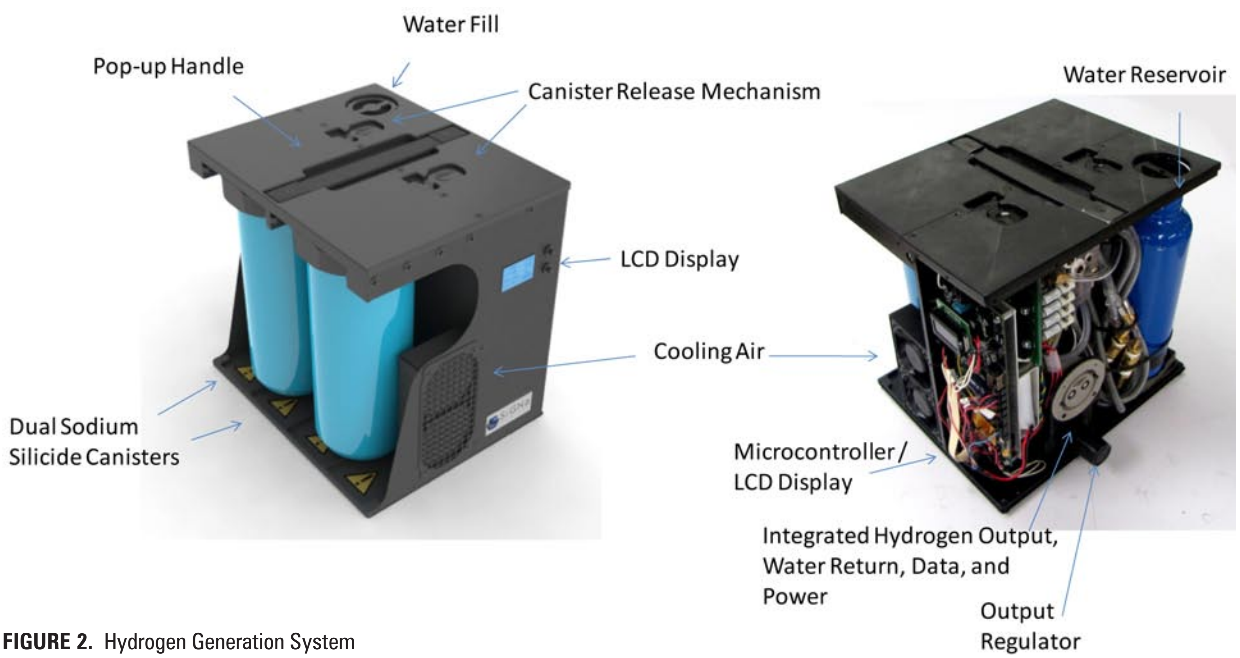

FIGURE 2. Hydrogen Generation System

The water distribution network is almost exclusively required for re-start conditions. Systems using this micro-nozzle manifold were shown to rapidly restart after storage at room temperature for seven days after first reacting 80% of powder.

Control

A predictive proportional-integral-derivative control system was developed to generate hydrogen at a near constant pressure even when using two canisters in parallel controlled via a single water

FIGURE 3. NaSi-Based Hydrogen Generation System with 300 W Hybrid Proton Exchange Membrane Fuel Cell System

FIGURE 4. Electric Bicycle

pump. By using calibrated pump data in conjunction with a measurement of the change in pressure over time (dp/dt), the microcontroller estimates the actual hydrogen flow. The hydrogen generation system also indirectly measures hydrogen flow rate by monitoring the fuel cell electrical current. However, pump data and pressure measurements have proven sufficient to control the pressure to within approximately +/- 5 psi at a nominal pressure of 30 psi.

Water Pump System

In addition to active pump control, SiGNa has developed a passive, disposable, orientation-independent water pumping system and water reservoir within the hydrogen cartridge. This system has demonstrated a near constant hydrogen pressure of 3 psi for regulator-free, low-cost fuel cell operation. This has only been tested on a smaller cartridge with a capacity of 30 liters - although it is anticipated to be scalable to the 1.2 liter vessel, this will not be demonstrated in the project.

Testing

Hundreds of tests and thousands of hours of hydrogen generation have been performed over the course of the project. Hydrogen yield is reliably at or near the theoretical maximum of 9.8 wt%. A combined water/powder energy density of over 1,300 Wh/kg LHV was achieved. In addition, an advanced sodium silicide mixture was shown to yield over 1,600 Wh/kg LHV and over 1,854 Wh/kg when recirculating 50% of the fuel cell waste water.

Conclusions and Future Directions

Sodium silicide is capable of controlled hydrogen flow for a range of portable applications. A number of implementation issues that have plagued other hydrolysis systems – particularly impacting restart capability – have been resolved. All results continue to indicate that sodium silicide is capable of near-term commercialization while providing a hydrogen source that is safe and easy to use. The balance of work in this project will be focused in the following areas:

- Final testing and verification of the hydrogen generation system.
- Continued testing on larger powder quantity runs to optimize control characteristics and minimize water usage.
- Continued testing and improvements on the hydrogen generation control system.
- Operation of the hydrogen generation system by a fuel cell system developer for independent performance verification.

Special Recognitions & Awards/Patents Issued

1. Patent Application Filed: Andrew Wallace, John Melack, Michael Lefenfeld, Hydrogen Generation Systems Utilizing Sodium Silicide and Sodium Silica Gel Materials, Patent Application, March 30, 2010, EFS ID: 7319440, International Application Number: PCT/US10/29257.

2. Received Commercial Development Contract for Micro-Fuel Cell Hydrogen Generation Cartridge.

FY 2010 Publications/Presentations

1. NaSi Hydrogen Generation for Portable Fuel Cell Systems, Small Fuel Cells, April 12-13, 2010.

2. DOE Annual Review, May 2010.