

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

**PAPER FOR THE NHA ANNUAL U.S. HYDROGEN
CONFERENCE March 18 – 22, 2007**

**HYDROGEN TECHNOLOGY RESEARCH AT THE
SAVANNAH RIVER NATIONAL LABORATORY, CENTER
FOR HYDROGEN RESEARCH (CHR) AND THE HYDROGEN
TECHNOLOGY RESEARCH LABORATORY (HTRL)**

E. T. Danko¹

1.0 Introduction

The Savannah River National Laboratory (SRNL) is a U.S. Department of Energy research and development laboratory located at the Savannah River Site (SRS) near Aiken, South Carolina. SRNL has over 50 years of experience in developing and applying hydrogen technology, both through its national defense activities as well as through its recent activities with the DOE Hydrogen Programs. The hydrogen technical staff at SRNL comprises over 90 scientists, engineers and technologists, and it is believed to be the largest such staff in the U.S. SRNL has ongoing R&D initiatives in a variety of hydrogen storage areas, including metal hydrides, complex hydrides, chemical hydrides and carbon nanotubes. SRNL has over 25 years of experience in metal hydrides and solid-state hydrogen storage research, development and demonstration. As part of its defense mission at SRS, SRNL developed, designed, demonstrated and provides ongoing technical support for the largest hydrogen processing facility in the world based on the integrated use of metal hydrides for hydrogen storage, separation and compression.

The SRNL has been active in teaming with academic and industrial partners to advance hydrogen technology. A primary focus of SRNL's R&D has been hydrogen storage using metal and complex hydrides. SRNL and its Hydrogen Technology Laboratory have been very successful in leveraging their defense infrastructure, capabilities and investments to help solve this country's energy problems. Many of SRNL's programs support dual-use applications. SRNL has participated in projects to convert public transit and utility vehicles for operation on hydrogen fuel. Two major projects include the H₂Fuel Bus and an Industrial Fuel Cell Vehicle (IFCV) also known as the GATORTM. Both of these projects were funded by DOE and cost shared by industry. These are discussed further in Section 3.0, Demonstration Projects.

In addition to metal hydrides technology, the SRNL Hydrogen group has done extensive R&D in other hydrogen technologies, including membrane filters

¹ Washington Savannah River Company (WSRC), Savannah River National Laboratory (SRNL), Bldg. 773-41A, Aiken SC 29808.

for H₂ separation, doped carbon nanotubes, storage vessel design and optimization, chemical hydrides, hydrogen compressors and hydrogen production using nuclear energy. Several of these are discussed further in Section 2, SRNL Hydrogen Research and Development.

2.0 SRNL Hydrogen Research and Development

Hydrogen Storage

The SRNL Hydrogen Technology Research Laboratory has extensive expertise in a variety of hydrogen related technologies including hydrogen storage. As an example of SRNL's hydrogen storage technology, metal hydrides absorb hydrogen when cold, store it below atmospheric pressure, and release it only when heated. This special group of metals provides a safer, more cost-effective method of storing, separating, pumping and compressing hydrogen. Potential applications exist in the transportation and energy industries, such as, hydrogen recovery from gas mixtures and hydrogen storage for alternative fuel vehicles.

SRNL continues to play a major role in the latest hydrogen research activities and developments. Besides the work on conventional low-pressure metal hydride materials for hydrogen storage, the SRNL hydrogen group is also involved in research on new higher capacity materials such as complex hydrides (borohydrides and alanates), carbon nanotube materials and hollow glass microspheres (Figures 1, 2 and 3). As research in the hydrogen storage field advances, there is a need to evaluate and analyze new, emerging technologies. With its many years of hydrogen experience, SRNL is in an excellent position to advise the DOE and other governmental and industrial entities on the merits of these high-potential hydrogen storage options. The SRNL Hydrogen Program group has a good working relationship with many of the leading researchers and research institutions in the area of hydrogen storage. For example, SRNL researchers play a key role in the DOE Hydrogen Program "Grand Challenge" as a partner in the Metal Hydride Center of Excellence (MHCoE) to advance hydrogen storage technology. Current research conducted at SRNL is at the forefront to advance the characteristics of these materials to achieve the optimum performance in hydrogen storage capacity.

Hydrogen is the lightest element known. Several options exist for storing hydrogen; these include compressed gas, cryogenic liquid, or a solid matrix. Gravimetric and volumetric densities of storage systems have proven to be low as compared to fossil fuels. Further research into complex hydrides will most likely prove that they will exhibit higher storage capacities than that of metal hydrides. Complex hydrides, such as NaAlH_4 are fairly new to industry and have exhibited reversible hydrogen storage properties and promising storage capacities. Research on these materials have shown that the decomposition temperatures of these may be lowered by using special manufacturing techniques such as high energy ball milling and by doping the materials.



Figure 1
Alanate Material

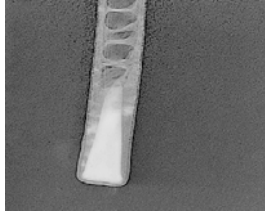


Figure 2
Carbon Nanotubes



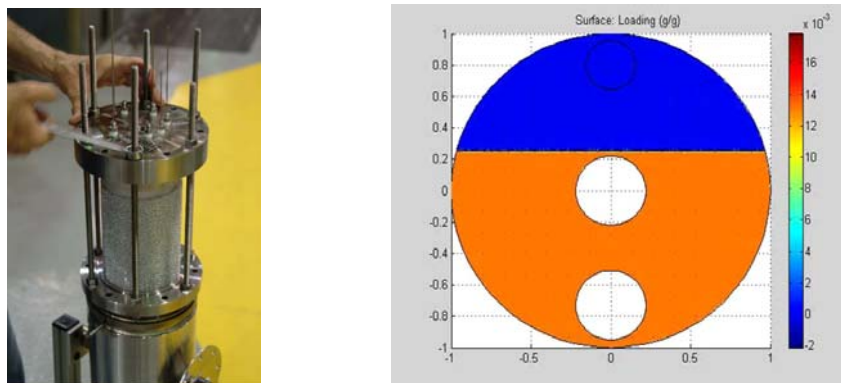
Figure 3
Hollow Glass Microspheres

Metal hydride beds are used extensively at SRS for tritium processing. They are also an important technology for hydrogen storage for commercial applications. The performance of a metal hydride storage system is influenced by a variety of factors, including process conditions, physical design, reaction kinetics, and transient heat and mass transfer in the bed. At the Savannah River National Laboratory, a variety of mathematical models have been developed that predict the basic performance of metal hydride systems. However, most of these models have either restricted themselves to steady-state conditions or have made extensive simplifying assumptions in an attempt to predict the complex behavior of the system. In order to predict heat and mass transfer in metal hydride systems, one must also deal with gas/solid interactions, phase changes, heats of reaction, material expansion, and a host of other phenomenon occurring simultaneously within the system.

Furthermore, the thermophysical properties of metal hydrides, such as thermal conductivity, specific heat, and particle diameter, are dependent on the reacted fraction (i.e. the solid solution phase has different properties than the hydride phase). Many of these properties can be predicted by conducting controlled experiments that measure “effective” bed properties and correlate them to the design and operating conditions. Inclusion of these properties into a versatile transient model that can accurately predict the behavior of metal hydride systems to a variety of design changes would be a very valuable tool for both future applications at SRS and commercial hydrogen applications.

Several of the key areas that need further development in order to arrive at such a tool is the powder, or particle-to-particle, heat transfer and metal hydride bed design optimization. It is known that the absorption and desorption of hydrogen are controlled by the low thermal conductivity of the metal hydride bed. An example of a metal hydride heat transfer experiment apparatus is shown in Figure 4. Even though these systems involve metals, they are in the form of fine powders, which are poor conductors. Many attempts have been made to improve the effective thermal conductivity of metal hydride powders. Designers have added a variety of heat transfer fins into the beds and have reduced the bed diameters to minimize the problem. None of these attempts have been totally successful. Scientists at SRNL have demonstrated the use of porous metal foams within metal hydride containers, which has led to considerable improvement in the overall heat transfer

characteristics of the hydride beds. However, a fundamental basis for this improvement and a means of characterizing the effective bed thermal conductivity under a variety of design and operating conditions have not been fully determined. Without this fundamental understanding, further improvements and optimizations to existing hydride systems, as well as adaptations to new systems and designs, will be difficult and inefficient.



2D and 3D Mass and Heat Transfer Models

Figure 4. Metal Hydride Heat Transfer Experiment

The Savannah River National Laboratory has been working with the other DOE labs and industry partners as part of the “Grand Challenge” Center of Excellence for hydrogen storage in the area of complex metal hydrides. The goal of the Grand Challenge is in the next 5 years to develop a hydrogen storage system that meets or exceeds the DOE 2010 goal for automotive applications [1]. These goals include system costs, refueling times, volumetric and gravimetric storage densities and energy efficiency. SRNL has the expertise and the capabilities to take on this aggressive challenge.

SRNL is currently conducting studies under the auspices of the International Partnership for a Hydrogen Economy (IPHE) program on the fundamental safety testing and analysis of hydrogen storage materials and systems [2]. Hydrogen is seen as the future energy storage media due to its inherent cleanliness upon oxidation and its ready utilization in fuel cell applications. To make safe and commercially acceptable systems, it is important to understand, quantitatively, the risks involved in using and handling these materials and to develop the appropriate safety systems. Researchers at SRNL have outlined a program that will seek to understand the physical risks involved in synthesis, handling and utilization of these materials as hydrogen storage media as well as development of methods to mitigate these risks which would result in commercially acceptable high density hydrogen storage system designs. The objective of this study is to fundamentally understand the safety issues regarding solid state hydrogen storage materials by

conducting standardized materials testing, chemical kinetics, risk mitigation, and prototype system testing.

Hydrogen Separations

Ongoing defense work has led to SRNL's broad experience in the area of hydrogen separation. SRNL has developed a new patented technology for separating hydrogen from other gases particularly carbon monoxide and other hydrocarbon combustion products [3]. The process makes use of a new class of composite materials referred to as "sol-gel metal hydrides". These materials have the ability to absorb hydrogen but also to restrict other gases such as carbon monoxide. Applications of this technology to commercial hydrogen production and separation systems are being investigated. A "thermal-swing" process utilizing this new composite material is believed to have significant advantages over traditional "pressure-swing" processes, especially on lower hydrogen containing feed streams. These lower hydrogen content feed streams are typically found in many biological hydrogen production processes. SRNL also has ongoing R&D on a new class of metallic and metallic oxide membranes that have the potential to overcome the limitation of many of today's current hydrogen membrane materials.

Hydrogen Production

In the area of hydrogen production, SRNL is currently involved in programs directed to achieve the goal of a hydrogen economy [4]. In order for the United States to move toward a hydrogen economy, hydrogen will need to be produced from a variety of primary energy sources, including: renewables, fossil fuels (with carbon sequestration) and nuclear energy. Hydrogen production from nuclear energy can provide a significant portion of the future hydrogen demand. To meet the demand of a hydrogen economy, safe and cost-effective methods for producing and distributing large quantities of hydrogen to supply a major portion of the national energy and transportation needs will be required [5]. SRNL has led a team of industry, academia and consultants for a project funded by the U. S. Department of Energy, Nuclear Energy to perform a three year study of the production of hydrogen from nuclear energy with emphasis on hydrogen infrastructure issues. The project was successfully completed in December 2005; the final report is available on the Department of Energy, Office of Nuclear Energy, Nuclear Energy Research Initiative (NERI) website.

Hydrogen Production Methods

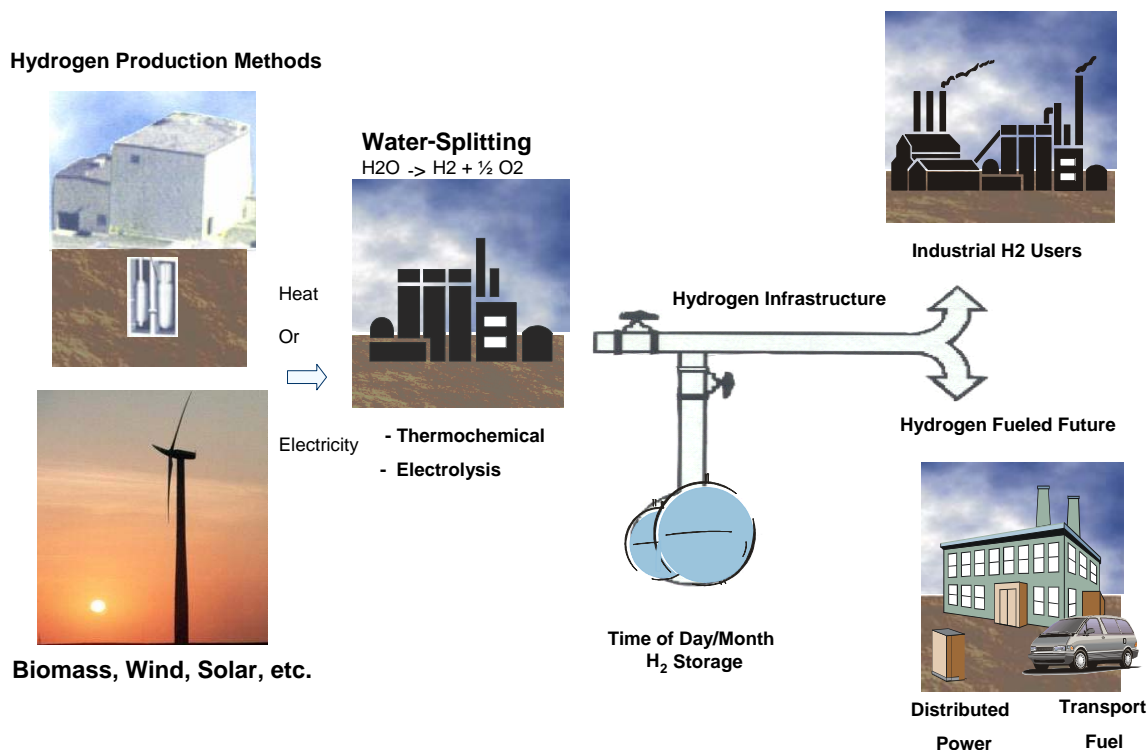


Figure 5. National Test Bed for a Hydrogen Economy

Figure 5 illustrates how a potential Hydrogen Future might appear. Heat would be generated by a next generation, fail-safe, nuclear power plant and directed to the thermochemical processing plant to produce hydrogen through a series of chemical reactions. Biomass, wind and solar power are other options that could be considered to provide energy as a source to produce heat. Thermochemical processes have the potential to produce hydrogen from water at higher efficiencies than conventional and even high temperature electrolysis processes. The hydrogen could then be stored above or below ground or provided as needed directly to industrial hydrogen users or to supply a hydrogen fueled future for distributed power or for transport fuel. A hydrogen pipeline would be the means to carry the hydrogen to its destination.

SRNL is also working to further develop the Hybrid Sulfur (HyS) process that was originally proposed by Westinghouse Electric Corp. in 1973 as an efficient way to produce hydrogen by splitting water using high temperature heat and electric power. This process is a two-step, hybrid, thermochemical cycle that is based on sulfur chemistry and represents the simplest thermochemical hydrogen process identified to date. HyS process streams contain only water, hydrogen, oxygen, and/or sulfur compounds. SRNL has been working since 2003 to develop the HyS process for the Department of Energy Office of Nuclear Energy, Science & Technology's (DOE-NE) Nuclear Hydrogen Initiative (NHI). The key issue continues to be the scale-up and cost of the electrolyzer, which distinguishes the HyS from other sulfur cycles like the Sulfur-Iodine. SRNL's electrolyzer is based on modified commercial PEM electrolyzer technology. The intent is to leverage PEM fuel cell and electrolyzer advances to develop a low-cost, SO₂ anode-depolarized

cell capable of achieving cell voltages of <600 mV/cell at current densities of >500 mA/cm². The overall, net thermal efficiency of SRNL's HyS process is estimated to be about 45-55% (HHV basis), depending on electrolyzer performance. This work being performed at SRNL will assist the DOE-NE in selecting which thermochemical cycle will ultimately be developed for integration with an advanced nuclear reactor by determining the true potential of the HyS process.

Hydrogen Sensors

SRNL has done extensive research and development on hydrogen sensors. SRNL's Sensors and Analyzers Technology Group has developed several sensing platforms to meet SRS needs for hydrogen processing and storage. Raman spectroscopy using fiber optic probes allows the quantification of hydrogen isotopes. This system has been demonstrated in a cryogenic separation process at SRS. Other probes use the surface plasmon resonance effect to detect hydrogen through optical changes induced in a thin palladium film by hydrogen uptake. Low-ppm detection limits have been achieved in the laboratory. Miniature mass spectrometers are being developed which will give millisecond measurements of hydrogen isotopes in process environments with minimal intrusion. This work has benefited greatly from pulse-counting methods originally developed at SRNL for radiological measurements.

3.0 Demonstration Projects

The Center for Hydrogen Research (CHR) located in Aiken, SC, the Savannah River National Laboratory (SRNL) and Proton Energy Systems have teamed to develop a regenerative fuel cell that will have the capability to provide back up power to the hydrogen laboratory in the event of a power outage. The project is funded by the DOE Office of Electricity Office of Electricity Delivery and Energy Reliability and the project goals are to 1) Demonstrate feasibility of using metal hydride storage in a regenerative fuel cell backup power system. 2) Develop an integrated system architecture that supports commercialization of this technology. 3) Provide an educational outreach function in a world class hydrogen research facility.

The H2Fuel Bus Project involved several academic and industrial partners whose goal was to modify an all electric transit bus to run as a hydrogen-electric hybrid vehicle. This bus had double the range of the all electric vehicle and still had virtually zero emissions relative to a diesel bus. The H2Fuel Bus used an engine-generator set running on low-pressure hydrogen stored on metal hydride beds [6]. The SRNL Team was tasked to develop the hydrogen storage system for the H2Fuel Project. To meet the vehicle's hydrogen delivery rate and rapid recharging requirements a new design for the metal hydride system had to be designed. SRNL scientists and engineers developed a new patented, high-heat-transfer vessel that allowed the hydrogen storage system to meet and even exceed its requirements. Several years later in one of the Site's defense applications, a similar need to improve the heat transfer in one of our separation units was identified. The prior work on the H2Fuel Bus storage system led the researchers to the solution. The SRNL solution led to a 50% reduction in the number of units required for the operation and a cost savings of over \$20 million [7].

The H2Fuel Bus shown in Figure 6 uses a hybrid power system consisting of a hydrogen-fueled internal combustion engine in series connected to batteries and an electric motor. This project demonstrated the world's first hybrid hydrogen electric transit bus. It achieved double the range of the all electric vehicle and more than twice the energy efficiency of a diesel bus. The hydrogen IC engine had virtually zero emissions [8]. The Blue Bird Body Company, a leading bus manufacturer, provided the transit bus incorporating an electric drive train supplied by Westinghouse Electric Corporation's Automotive Systems. The Savannah River National Laboratory designed and in collaboration with Hydrogen Components Inc. (HCI), built the onboard hydrogen storage system based on advanced low temperature metal hydride technology developed as part of the Savannah River Site's national defense mission. The City of Augusta, Georgia operated the bus after successful testing and demonstration. The U.S. Department of Energy was the project sponsor.

The metal-hydride-based storage system had a capacity of 15 kg of hydrogen. The overall storage system weighed 2000 kg, making it one of the largest vehicle hydrogen storage systems ever built. It operated at 100 psig and used waste heat from an internal combustion engine at 80°C. The bus operated successfully in transit service in Augusta, Georgia, and was later transferred to Las Vegas, Nevada as part of a DOE hydrogen demonstration program. Figure 7 shows one of two metal hydride hydrogen storage assemblies used in the bus.



Figure 6
World's first Hydrogen Hybrid
Electric Bus (Augusta, GA)

Specifications

Length	33 ft.
Wheelbase	193 in.
Gross Vehicle Weight	33,000 lbs (15,000 kg)
Passenger capacity	27 seated
Electric Propulsion	230 HP AC (170 kW)
Range	120 miles
Fuel consumption	7.5 mpg equivalent
Braking	Regenerative
Emissions	CO near 0
	NO <1ppm

Mission

Convert a battery-powered transit bus to a hydrogen-powered hybrid bus, using metal hydrides to store hydrogen.

Project Team

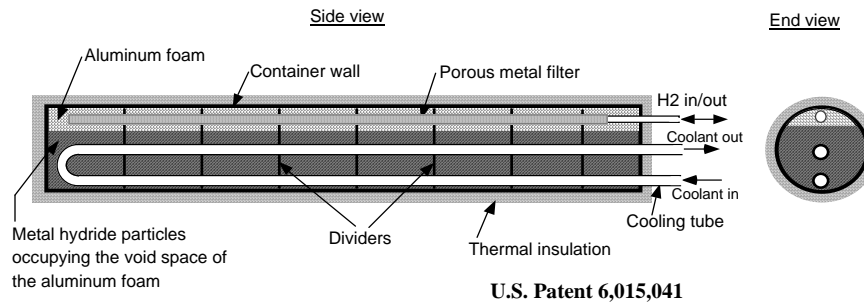
U.S. Department of Energy
Savannah River National Laboratory
Southeastern Technology Center
Georgia Tech Research Institute
Atlanta-Richmond County Public Transit
Hydrogen Components, Incorporated
Blue Bird Body Company



Figure 7
World's largest mobile metal hydride storage bed

Project Description

Road driving tests started April 1997
Hydrogen storage performed better than expected
Hybrid power train improved energy efficiency
Hydrogen doubled the operating range of batteries
Hydrogen engine demonstrated near-zero emission (No < 0.2ppm)



High performance tubular design permits compact storage and rapid refueling

Figure 8. Metal Hydride Bed

Figure 8 illustrates a cut away view of the metal hydride bed. This basic design was utilized in both the H2Fuel Bus and the IFCV “GATOR” project that is discussed in more detail below. The container is divided into sections that are fitted with metal foam and filled with metal hydride particles to occupy the void space within the metal foam. As shown, metal tubing is integrated into the assembly to provide heating and cooling as required.

The Industrial Fuel Cell Vehicle (IFCV) is shown in Figure 9.

Following the successful H2Fuel Bus Project, SRNL worked with several academic and industrial partners in developing an industrial fuel cell vehicle. The goal of this program was to develop and demonstrate two fuel cell vehicles running on direct hydrogen [9]. The specific vehicles used were Deere and Co. GATOR™ vehicles with the fuel cell systems supplied by Energy Partners L.C.² The project objective was to offer the small industrial vehicle sector an alternative to limited-range, battery-electric vehicles [10]. To ensure the utmost safety for indoor applications, SRNL was asked to develop a low-pressure hydrogen storage system for these vehicles. The project team was able to develop and demonstrate two GATOR vehicles running on low-pressure hydrogen. The vehicles demonstrated a 50% improvement in fuel-to-wheel efficiency when compared to similar internal combustion engine vehicles and a 100% improvement in range when compared to battery-electric vehicles. During the course of the vehicle development the SRNL team was able to reduce the weight of the hydrogen storage system by 15% and lower its material costs by over 50%.

Another objective of the overall program was to develop and validate a compatible hydrogen generator system that could ultimately be used to fuel fleets of IFCV's. An electrolyzer developed by Teledyne Energy Systems was used to refuel the vehicle; tests were performed at the University of South Carolina and York Technical College. The project objective was to offer the small industrial vehicle sector an alternative to limited-range battery-electric vehicles.

² Currently known as Teledyne Energy Systems due to a merger.



Figure 9
Fuel Cell Vehicle w/MH Storage

Mission

Develop a fuel cell vehicle with onboard metal hydride storage for near-term niche markets such as airports, outdoor maintenance, warehouses, etc.

Project Team

U. S. Department of Energy
Savannah River National Laboratory
Southeastern Technology Center
John Deere and Company
Teledyne Energy Systems
University of South Carolina
York Technical College

Project Description

Phase I – Feasibility Study, completed Jan. 1998
Phase II/III – Develop and Validate Technology,
December 31, 2000

Benefits

Zero Emissions
Same Performance as Gasoline Vehicles
Out Performs Battery Vehicles

4.0 Summary and Path Forward

While SRNL has been successful in sharing its 50 years of hydrogen expertise with other government, industrial and academic entities over the past several years, the future for SRNL's hydrogen initiatives and the hydrogen economy looks even brighter. Aiken County built and operates the new Center for Hydrogen Research (see Figure 10). This new Center, a 60,000 square foot facility, is dedicated to hydrogen research and development. Construction was completed during December 2005 and the facility was dedicated in February 2006. SRNL and its regional partners occupy this facility under a lease agreement. One-half of the laboratory, known as the Hydrogen Technology Research Laboratory (HTRL), is occupied by the SRNL hydrogen group to continue its ongoing efforts in hydrogen storage, separation, sensors and production technology development. The other half of the facility is available as a user-facility to encourage collaborative efforts between SRNL and other scientists from industry, academia and other government agencies. Additional plans for the facility are underway to include a hydrogen refueling station, a small fleet of hydrogen vehicles and a stationary fuel cell for some of the facilities auxiliary or backup power requirements.



Figure 10 Center for Hydrogen Research

The Savannah River Site and Savannah River National Laboratory have a long history of providing for our country's national security needs. Due to our increasing dependence on limited foreign oil reserves, SRNL has expanded its security role to include energy security to address future energy security needs in the United States. SRNL is seeking academic, industrial and other government agency partners to help meet our national and global energy needs.

References:

- [1] Report of the National Research Council, the Hydrogen Economy: Opportunities, Costs, Barriers and R&D Needs, 2004.
- [2] D. Anton, M. Fichtner, D. Mosher, N. Kuriyama, E. Akiba, R. Chahine, D. Dedrick, Fundamental Safety Testing and Analysis of Hydrogen Storage Materials & Systems, paper presented at the 2nd International Conference on Hydrogen Safety, San Sebastian, Spain Sept. 11-13, 2007.
- [3] Heung, Leung (SRTC), 2003 Annual Merit Review and Peer Evaluation Report, Project #16, Encapsulated Metal Hydride for H₂ Separations.
- [4] Motyka, T., Zidan, R., Summers, W.A., Hydrogen Storage: The Key Challenge Facing a Hydrogen Economy, paper for World Hydrogen Energy Conference, March 2004.
- [5] Danko, E., Summers, W. SRTC Research into Hydrogen Production from Nuclear Energy. *National Hydrogen Association Quarterly Newsletter* 9(2), Spring 2004.
- [6] Heung, L. K.: On-Board Hydrogen Storage System Using Metal Hydrides, HYPOTHESIS II Conference, Grimstad, Norway, August 18-22, 1997, pp 251-256.
- [7] Summers, W.A., T. Motyka, and E. Danko. Metal Hydride Technology – A Technology Transfer Success Story. Hydrogen storage paper for Department of Energy, Office of Industrial Technology, October 2001.
- [8] Westinghouse Savannah River Company Report WSRC-TR-98-00385, Final Report for the H₂Fuel Bus, W.D. Jacobs, L.K. Heung, T. Motyka, W.A. Summers, J.M. Morrison, January 1999.
- [9] Fuchs M. et al.: Performance of 3rd Generation Fuel Cell Powered Vehicle #2 with Metal Hydride Fuel Storage, European PE Fuel Cell Forum, Luzern, Switzerland, July 2-6, 2001.
- [10] Danko, E. SRTC's Low-Pressure Metal Hydride Hydrogen Storage System: GATOR. *National Hydrogen Association Quarterly Newsletter* 7(3), Autumn 2002.