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ABSTRACT
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NASA HYDROGEN RESEARCH AT THE UNIVERSITY OF FLORIDA

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January 2004

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The research program at the University of Florida focuses on the following areas:

- New and improved hydrogen production processes
- Hydrogen leak detection via laser instrumentation
- Hydrogen leak detection via distributed micro-sensors
- Terrestrial and in-space cryogenic transport and storage
- High energy densified materials for hydrogen storage
- New propellants and cryofuels
- Education and outreach activities.

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NASA HYDROGEN RESEARCH AT THE UNIVERSITY OF FLORIDA

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ABSTRACT

In 2003 NASA’s Glenn Research Center awarded an 18-month, $7.92-million grant to Florida universities for hydrogen research. This program brings together researchers from Florida universities with NASA Glenn Research Center and NASA Kennedy Space Center to form a powerful partnership.

The research program at the University of Florida (UF) focuses on the following areas:

- New and improved hydrogen-production processes
- Hydrogen-leak detection via distributed micro-sensors
- Hydrogen-leak detection via laser instrumentation
- Terrestrial and in-space cryogenic transport and storage (CTS)
- Education and outreach activities

Exactly 22 Co-Principal Investigators and a number of post-docs and graduate students are actively working on 15 research tasks. The objectives and the current accomplishments of their research projects are summarized below.

A mobile demonstration unit for testing and education is being built for one of the hydrogen-production processes and the plan is to demonstrate it at or near Kennedy Space Center after its completion.

INTRODUCTION

The University of Florida has developed a very strong hydrogen-technology base with two consecutive NASA grants. The research projects described in this paper are for the FY 03 grant. The goal of these endeavors is to continue the leading-edge research and technology development in the areas of hydrogen-production processes, distributed sensors and laser instrumentation for hydrogen-leak detection, and cryogenic transport and storage solutions.

Peggy Evanich, director of space research at UF, is the PI for the grant. Exactly 22 Co-Principal Investigators and a number of post-docs and graduate students are actively working
on 15 research tasks. The chart below provides the grant budget distribution and its comparison to the previous grant.

![Graph showing grant budget distribution]

Figure 1: NASA Hydrogen Research Grant Budget

The budget for this research grant includes 15 research projects, education and outreach activities, system and trade studies, and project management.

The four research thrusts, their faculty leaders, as well as outreach activities are detailed below.

1. **Hydrogen production; Dr. H. A. Ingleby**
   Under the previous grant three hydrogen-production processes were established for research and development – one a collaborative effort between UF and the University of South Florida. The goal for the current grant is to demonstrate the feasibility of each hydrogen-production process by testing the concepts at a larger scale and performing system and trade studies.

   A local hydrogen production may eliminate some of the traditional hazards of NASA’s use of hydrogen. For example, for each space-shuttle launch, hydrogen is shipped to the Kennedy Space Center (KSC) by Air Products, Inc. from their New Orleans facility. This means some 50 tractor-trailers must drive approximately 700 miles to deliver hydrogen for every launch. By creating a local hydrogen-production facility, the safety hazards of long-distance transportation can be avoided and the cost of hydrogen will be reduced.
2. **Distributed sensors for hydrogen-leak detection;** Dr. M. Law
The distributed sensors for hydrogen-leak detection are small, low-cost, low-power sensors that can communicate with each other in a node matrix, detecting hydrogen leaks along hydrogen-transport piping and around storage vessels. The goal is to test and demonstrate these sensors in a realistic environment while also bringing them closer to production and commercial viability for eventual use in the operating environment.

3. **Laser instrumentation for hydrogen-leak detection;** Dr. D. W. Hahn
Research in laser instrumentation for hydrogen-leak detection includes Raman spectroscopy, Raleigh and Mei light scattering techniques as well as work on laser-induced breakdown spectroscopy (LIBS). The goal is to develop a unit that can be used for field testing.

4. **Cryogenic transport and storage (CTS);** Dr. J. Klausner
Research in terrestrial and in-space cryogenic transport and storage focuses on optimal solutions for the transportation and storage of cryogenic fluids at NASA's KSC. The research also addresses technical issues regarding in-space transport and storage of cryogenic hydrogen.

5. **Outreach;** Dr. H. Beck
A hydrogen-technology database and a website are being developed as part of the education and outreach activity. A graduate course on hydrogen technology at UF has been developed and is being offered to graduate students this semester.

**GOALS AND ACCOMPLISHMENTS OF THE RESEARCH**

1. **Hydrogen Production**

*The Ammonia -Water Combined Power and Refrigeration Cycle, Co-PI: Dr. H. A. Ingle, P.E.*

Hydrogen production via water electrolysis is a proven technology, but is infeasible due to the high cost of energy. To reduce such costs, the ammonia-water combined power and refrigeration cycle produces electricity by using low-temperature heat sources, waste heat, or solar energy. The project goal is to design and construct a combined-cycle mobile test facility that generates 5 kW of electricity from a low-temperature heat source, and use this electricity to produce 18 L/min of hydrogen by using an electrolysis unit. The mobile facility will demonstrate the feasibility of this process and also serve as an educational tool to display hydrogen production via low-temperature heat source and the usage of hydrogen produced in a fuel cell. The preparations for installation have begun. The 40x60-ft trailer that will house the combined-cycle process was designed and ordered, and all required equipment has been sized, selected, and ordered.
Rectenna, Co-PI's: Dr. Y. Goswami (UF), and Dr. L. Stefanakos (USF), Dr. K. Buckle (USF), Dr. S. Bhansali (USF), Dr. T. Weller (USF)

The idea behind the rectenna is to absorb incident electromagnetic radiation (i.e. solar radiation) efficiently by using nano scale antenna arrays, then to rectify the electricity by using high-frequency metal-insulator-metal (MIM) tunneling diodes.

The project is a collaborative effort with USF but this research actually began at UF in 1970 and was patented. Research was suspended, however, because the project required inventions in the materials area. However, recent advances in nanotechnology have made it feasible to resume work on this project. As part of the collaboration, researchers at USF have built 74 Gz slot antennas and MIM diodes for testing. The project aims to reduce the cost of generating electricity to make hydrogen production via electrolysis feasible.

Advanced Protonic Conductors, Co-PI: Dr. E. D. Wachsman

This project aims to demonstrate the feasibility of producing hydrogen from hydrocarbon-based fuels using an advanced proton-conducting membrane. Such membrane reactors can be used to produce hydrogen from hydrocarbon feed stocks – from natural gas to coal to a variety of hydrocarbon-containing waste streams such as landfill gas and swamp gas. The research focus for this phase is to develop thin-film proton-conducting membranes on porous supports and to advance the fundamental understanding of these materials. The anticipated result is to show high hydrogen fluxes through these thin, supported membranes. Several membrane formulations have been developed and the testing of these membranes is in progress (see Figure 2 below). Tubular membrane reactors were manufactured for demonstration.

Figure 2: Single closed-end hydrogen membrane
2. Distributed Sensors for Hydrogen-Leak Detection: Co-PI's: Dr. M. Law, Dr. F. Ren, Dr. S. Peartion, Dr. R. Fox, Dr. K. O, Dr. J. McNair, Dr. J. Lin

Hydrogen storage and transport requires careful leak monitoring to prevent dangerous explosions and fires. The research focus here is to develop a set of sensors small enough to be mounted on hydrogen-transport piping lines and on storage vessels. These sensors also need to be inexpensive, consume little power, and operate at room temperature. These sensors would detect the hydrogen leakage and transmit the detected signal to the command center to alert operators for the location and magnitude of the leak.

GaN- and ZnO-based sensors that can detect hydrogen at room temperature have been demonstrated (see Figure 3 below). The new focus is to build sensors with a wafer structure of high electron mobility transistor (HEMT), as shown in Figure 4, to employ field effect transistor (FET) concept to increase the detection response. The remote communication among the sensors has been demonstrated, while modeling work, including the simulation of hydrogen leak diffusion is in progress.

![Figure 3: GaN Schottky Diode Based Wireless Hydrogen Sensor](image)

![Figure 4: AlGaN/GaN High Electron Mobility Transistor Based Sensor](image)
Sensing Hydrogen by Using Biological Assays, Co-PI: Dr. Z. H. Fan
This project’s goal is to develop a novel hydrogen sensor using an enzyme-catalyzed reaction and micro-fluidic technology. The anticipated benefits over state-of-the-art metal- (e.g. palladium) or alloy-based hydrogen sensors include the ability to operate at ambient temperatures, the ability to operate in background gases (e.g. nitrogen) due to the specificity of the enzyme, fast response time, and no recovery time.

3. Raman and Rayleigh/Mie Scattering for Hydrogen-Leak Detection, Co-PI’s: Dr. D. W. Hahn and Dr. J. E. Peterson
Detecting leaks of rocket propellants, notably hydrogen, is an ongoing area of concern for the space launch vehicles. To aid in safety and efficiency, remote leak-detection capabilities will enable standoff interrogation of various hydrogen-handling facilities, such as transfer lines and piping, as well as shuttle-launch pad detection. This research is developing diagnostic tools for portable, remote hydrogen-leak detection using laser-based techniques such as Rayleigh / Mie light scattering, Raman spectroscopy, and laser-induced breakdown spectroscopy (LIBS). The research focuses on Rayleigh / Mie / Raman integration using temporal and spectral data analysis in combination with pulsed laser excitation to discriminate from background contaminants and to optimize leak detection at its source. The overall project goal is to develop a portable laser instrument package for field evaluation. The optical layout of the field-testable unit has already been completed (see Figure 5 below), and the required laser unit and components have been ordered. Preparations for the installation have already begun.

Figure 5: Raman and Rayleigh/Mie field instrument optical layout.
4. Cryogenic Transport and Storage (CTS):

*Terrestrial Cryogenic Two-Phase Flow & Heat Transfer*, Co-PI’s: Dr. J. F. Klausner and Dr. R. Mei

Cryogenic fluids flowing through pipelines often operate in a two-phase flow regime. To design transport systems for two-phase flows, it is critical to accurately predict the pressure gradients and heat-transfer coefficients associated with the fluid and thermal conditions. The most reliable two-phase flow models for predicting pressure gradient and heat-transfer coefficients in pipe flow are specific to a particular flow configuration or flow regime. However, only sparse information on two-phase flow regimes with cryogenic fluids is available, and designers of cryogenic systems rely on generic flow-regime maps. Thus researchers need to collect flow-regime data on cryogenic fluids for a variety of operating conditions and gravitational environments. Data collected from this investigation can be used to explore the applicability of existing flow-regime maps to cryogenic fluids. The results will provide designers of cryogenic systems the means to identify the operating flow regimes. Extensive flow-regime pattern-recognition experiments have already been carried out and flow-regime maps are being constructed from these experiments. The figure below shows the process flow diagram of the cryogenic facility.

![Figure 6: Cryogenic Facility Flow Diagram](image-url)
Cryogenic Two-Phase Flow & Heat Transfer in Reduced Gravity, Co-PI’s: Dr. W. Shyy and Dr. J. N. Chung
The efficient and safe use of cryogenic fluids in thermal management, power and propulsion, and life-support systems during space missions involves the transport, handling, and storage of these fluids in reduced gravity. Due to the fluids’ low boiling points, two-phase flows are encountered in most cryogenic operations.

The problem’s complexity results from the intricate interaction of the fluid dynamics and heat transfer, especially when phase-change (boiling and condensation) is involved. Because of the large stratification in densities between the liquid and vapor phases, the reduced-gravity condition in space would strongly change the terrestrial flow patterns and accordingly affect the fluid’s momentum and energy-transport characteristics. This research focuses on addressing specific fundamental and engineering issues related to the microgravity two-phase flow and heat transfer of cryogenic fluids, which requires advanced numerical simulations in concert with validating experimentation. The research will provide cryogenic practitioners with analysis tools to address specific issues in the safe and efficient operation of liquid-hydrogen cryogenic transport systems in reduced gravity. The existing experimental set-up has been improved, and data collection and modeling work are in progress.

Chill-Down Process of Hydrogen-Transport Pipelines, Co-PI’s: Dr. R. Mei and Dr. J. Klausner
This research aims to empirically and computationally study the unsteady dynamics of a liquid-hydrogen wave front moving down a pipeline during chill-down mode and to develop a comprehensive computational model to predict the associated flow fields, thermal fields, and residence time. The group has already begun to:

- Study the dynamics of a propagating liquid-hydrogen wave front
- Measure the heat-transfer rate associated with film boiling beneath the wave front
- Investigate transient nucleate boiling heat transfer associated with liquid film flow
- Develop a comprehensive computational model to predict the flow and temperature fields associated with propagating liquid-hydrogen waves
- Develop engineering models for cryogenic practitioners to predict the required chill-down residence time under a variety of operating conditions

Composite Pressure Vessels for CTS, Co-PI’s: Dr. B. Sankar and Dr. P. Ijju
Honeycomb sandwich panels find a wide range of structural applications due to their relatively high strength and stiffness-to-weight ratio. Structural honeycombs are composed of two thin, stiff, strong sheets serving as the primary load-carrying elements and a thick layer of low-density cellular material to provide shear resistance and stiffness. In this research, interfacial mixed-mode fracture of the face-sheet and the core is evaluated both experimentally and analytically in environments similar to those encountered in cryo-tanks used in reusable launch vehicles. Interfacial fracture toughness tests are being performed at near-liquid-nitrogen temperature and room temperature to determine temperature effects on the critical strain energy release rate of the sandwich system. In addition to studying the interfacial fracture behavior of sandwich composites, it is necessary to understand the micro-cracking of face sheets that may cause hydrogen leaks. The results will be used to suggest efficient and safe designs for composite hydrogen-storage systems. Additional analysis
includes examining hydrogen-storage systems under more realistic loading conditions, and modeling progressive damage and permeability. Figure 7 shows a sample of a composite structure after fracture testing.

Figure 7: Composite structure: Zoom-in view of crack

**Zero Boil-Off (ZBO) Pressure Control, Co-PI: Dr. J. N. Chung**
A unique facet of storing liquid cryogens is that a sizable amount of heat will continually flow from the environment to the low-temperature fluid. Despite the fact that excellent multilayer insulations have been developed for storing cryogens, a finite amount of heat will always flow into the storage vessels, especially in the vicinity of supporting structures. As the heat accumulates, it will eventually vaporize a finite amount of liquid. Due to the large volumetric expansion from vaporization, the pressure in the vessel will significantly increase unless the vapor is exhausted from the vessel. Thus, excess vapor must continually be purged from the cryogenic storage tank. This is not efficient, and depending on the duration of storage, a significant amount of cryogens can be wasted. To preserve the cryogens in storage for a long space flight, an active heat-removal system is required to balance the heat that permeates the storage vessel. Such a system would eliminate the need to purge the cryogen vapor from the storage tank. A ZBO-system model is being developed to determine whether active mixing of the cryogen is required for ZBO and whether the benefits outweigh the complications. A comparison study between a sensible heat-transport system and a latent heat-transport system is being included in the model. An optimal latent heat-transport system is being designed to determine the appropriate degree of sub-cooling.

**Fluid Distribution for In-Space Cryogenic Propulsion, Co-PI: Dr. W. Lear**
This task’s ultimate goal is to enable the use of a single supply of cryogenic propellants for three distinct spacecraft propulsion missions: main propulsion, orbital maneuvering, and attitude control. A fluid-distribution system is sought that allows large propellant flows during the first two missions while still allowing control of small propellant flows during attitude control. Existing research has identified the probable benefits of a combined thermal management/power/fluid-distribution system based on the Solar Integrated Thermal Management and Power (SITMAP) cycle. A numerical and an experimental model are being constructed to predict the performance of such an integrated thermal management/propulsion
The numerical model and experimental apparatus will simulate an integrated thermal/power/fluid-management system based on the SITMAP cycle.

The theoretical and experimental results from these models will be used to develop a computerized design code that will provide design parameters for such a system, over a range of cooling loads, power generation, and attitude-control thrust levels. The performance gains and weight reduction will be compared to those of existing spacecraft systems. Experimental studies and numerical modeling of the SITMAP-based propellant distribution system are in progress.

**New Propellants and Cryofuels, Co-PI’s: Dr. N.S. Sullivan and Dr. J. Hamida**

The goal is to investigate the stability and cryogenic properties of solid propellants that are critical to NASA’s goal of realizing practical propellant designs for future spacecraft. The stability and thermal properties of a solid-hydrogen/liquid-helium stabilizer is being determined in a laboratory environment to design a practical propellant. Methods being explored include embedding atomic species and metallic nano-particulates in hydrogen matrices suspended in liquid helium. The methods of introducing metals into the hydrogen matrices are: (i) radio-frequency discharge dissociation of molecular hydrogen in the cryogenic injection path, and (ii) evaporation of metallic atoms from hot filaments in the hydrogen/helium gas stream into the condensation stream.

**Ortho-Para Hydrogen Ratiometry, Co-PI’s: Dr. N. S. Sullivan, Collaborator: Dr. D. Zhou**

This research entails the optimization of a thermal-conductivity cell designed to measure the ratio of the ortho and para hydrogen concentrations in gaseous samples. This method of ratiometry is based on the difference in the thermal conductivity of the two molecular species of hydrogen. The objective is to obtain fast, accurate measurement in a simple compact cell. Investigators are optimizing an electronic readout instrumentation to demonstrate the sensitivity, stability, and speed of the ratiometer’s response. New materials are also being explored for the development of high-efficiency ortho-para converters.

**High-Energy Densified Materials, Co-PI’s: Dr. G. G. Ihas, Dr. J. Graham**

The use of high-energy densified materials such as solid hydrogen doped with chemical species, like cryogenic fuel, offers the possibility of using a smaller volume of fuel to launch a given payload into orbit or to launch heavier payloads. One method is to embed certain metal atoms (aluminum or boron, for example) in solid hydrogen. It has been demonstrated theoretically that this results in a high-energy densified fuel. However these calculations ignore possible interactions between the metal atoms and the solid-hydrogen matrix. Moreover, these interactions, in general, have not been measured. The research goal is to build a cryostat in order to study how atomic species interact with solid hydrogen and what chemical species are produced. The equipment design has been completed and preliminary results on solid hydrogen doped with impurities at 2 and 4 degrees K have been obtained.
5. Outreach:

**Hydrogen-Technology Database and Website Development, Co-PI: Dr. H. Beck**

Using an existing, highly adaptable UF database methodology, a dynamic hydrogen-technology database with Web interface is being developed. The database will document and describe hydrogen-research activities carried out at UF – including all researchers involved, their research activities, refereed publications, and pertinent research data. The database will connect researchers and improve communications within the program and with external hydrogen and energy-research communities. The database framework has been completed and the majority of the existing data entry has already been completed. The Website is in progress.

**System and Technology Trade Studies, Consultant: Dr. D. Kirmsey**

System studies and trade studies for the Ammonia-Water Combined Power and Refrigeration Cycle will be performed by using advanced computer software tools, such as the ASPEN chemical process modeling software. This will be followed by the Advanced Protonic Conductors for Hydrogen Production project, when the required data is available.

By using well-structured trade methodologies it will be possible to select the most promising hydrogen production technologies for further research and development.

**OTHER ACTIVITIES**

Competing for other government and private funding opportunities by leveraging the NASA hydrogen grant is a continuing effort. The activities in this area include the following:

- Dr. E. D. Wachsman received two fuel-cell DOE awards ($1.25M)
- Dr. H. A. Ingley submitted a DOE proposal for H₂ education ($3M for all projects)
- Dr. J. Chung submitted a proposal to NASA on cryogenic boiling and two-phase flow in microgravity ($472K).
- UF and UCF partnered with Purdue on an NSF Science and Technology Center (STC) pre-proposal for hydrogen research.
- Two interdisciplinary teams were formed to respond to a DOE’s biomass solicitation ($10M for all projects).

The grants have also led to other results. Two invention disclosures have been submitted, and more than 15 publications have been published or are in preparation.