FINAL REPORT

Hydrogen Research at Florida Universities

NASA Grant NAG 3-2751

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Abstract

This final report describes the R&D activities and projects conducted for NASA under the six-year NASA Hydrogen Research at Florida Universities grant program. Contained within this report are summaries of the overall activities, one-page description of all the reports funded under this program and all of the individual reports from each of the 29 projects supported by the effort. The R&D activities cover hydrogen technologies related to production, cryogenics, sensors, storage, separation processes, fuel cells, resource assessments and education. In the span of six years, the NASA Hydrogen Research at Florida Universities program funded a total of 44 individual university projects, and employed more than 100 faculty and over 100 graduate research students in the six participating universities. Researchers involved in this program have filed more than 20 patents in all hydrogen technology areas and put out over 220 technical publications in the last two years alone. The NASA research grant has also led to the universities receiving over $6.336 million in additional funding from other federal agencies for research on twelve projects - all related to the NASA funded effort.

This six year hydrogen research program was conducted by a consortium of six Florida universities: Florida International University (FIU) in Miami, Florida State University (FSU) and Florida A&M University (FAMU) in Tallahassee, University of Central Florida (UCF) in Orlando, University of South Florida (USF) in Tampa, and University of Florida (UF) in Gainesville. The Florida Solar Energy Center (FSEC) of the University of Central Florida managed the research activities of all consortium member universities except those at the University of Florida. This report does not include any of the programs or activities conducted at the University of Florida.

Program Summary

Florida Solar Energy Center (FSEC) of the University of Central Florida (UCF) was funded by NASA-GRC in March 2002 to conduct research and manage this NASA research grant program. Soon after, a Request for Proposals (RFP) was issued to all of the universities in the State University System of Florida. A total of 37 proposals were received of which 30 were selected for funding. Selections were made following review by a FSEC Review Committee and by the NASA program managers at both Glenn Research Center (GRC) and Kennedy Space Center (KSC). For each of the selected projects, other than those at FSEC, formal contracts to the corresponding university were issued by the UCF Division of Sponsored Research. These university contracts were overseen by the FSEC program managers. Work at the participating universities began in the August to December 2002 time frame. Table I presents the list of the initial 30 projects and the principle investigators for each project. The listing is presented by projects under each university.

Table 1. Projects funded for the initial year. (Listed in alphabetical order of project titles).

Florida Solar Energy Center

- Analysis of Alternative Hydrogen Production Processes Liquid Hydrogen Production via Hydrogen Sulfide Methane Reformation - Huang, C; T-Raissi, A
- Development of Tribological Coatings for Cryocoolers - Dhere, N.
- Experimental Design & Evaluation of ZBO Cryogenic Systems - Baik, J.
- Hydrogen Education and Outreach – Schleith, S., Henzmann, A.
- Hydrides for Hydrogen Purification and Recovery - Slattery, D.
- Hydrogen Production via Photocatalysis - Linkous, C.
- Hydrogen Purification and Storage Using Lithium Borohydride - Linkous, C.
- Local Hydrogen Production via Catalytic Reformation of Fossil and Renewable Resources - Muradov, N., Smith, F.
- Photoelectrochemical Water Splitting for Hydrogen Production Using Multiple Bandgap Combination of Photovoltaic Cells and Photocatalyst. - Dhere, N.
- R & D Processes for Increasing the Fluid Density of Cryogenic Liquids - Baik, J.
- Safety and Monitoring Systems - Alternate Methods of Operating H_2 Systems During Start-up and Shutdown - Elbaccouch, M., Bain, A.
- System Analysis of Hydrogen Production and Utilization at KSC - T-Raissi, A., Gu, L., Huang, C., Robertson, T.
- Technoeconomic Analysis of the Use of Densified Propellants in Storage and Transportation Systems - Baik, J.

University of Central Florida

- Development of Cryogenic Actuator Materials for Switches, Seals and Valves - Vaidyanathan, R.
- Development of Hydrogen Gas Sensor with High Sensitivity and Selectivity Based on Doped Nanocrystalline-nanoporous Metal/Metal Oxides for Space Explorations – Seal, S.
- Metal Alloys for Hydrogen Recovery and Purification - Hampton, M.
- Novel Technique for the Detection and Location of Hydrogen Leaks – Sellar, G.
- Quasicrystalline Materials for Hydrogen Recovery and Purification - Hampton, M.
- Two-Stage Cryocooler Development for Liquid Hydrogen Systems - Chow, L., Kapat, J.

Florida State University

- Development of Optical Mass Gauging Systems - Van Sciver, S.
- Experimental and Numerical Investigations of Solid Hydrogen Particles in Liquid Helium - Van Sciver, S.
- Measurement of Transport Properties of Densified LH_2 and LO_2 - Van Sciver, S.

Florida International University

- Assessment of Florida's Biomass Resources for Hydrogen Production Using GIS – Ebadian, M., Tachiev, G., Srivastave, R., Philippidis, G.

University of South Florida

- By Product Hydrogen Production - Krakow, B., Stefanakos, E., Moore, G.

- Development of a Numerical Simulation Model for Thermo-Fluid Analysis and Design Optimization of Cryogenic Storage Systems with Zero Boiloff - Rahman, J.
- Electrochemical Catalytic Cell for the Production of Hydrogen from Various Fuel Stocks – Benson, R., Wolan, J.
- Hydrogen Gas Sensors by Surface Acoustic Waves - Bhethanabotla, V., Bhansali, S., Joseph, B.
- Hydrogen Liquefaction by Metal Hydride Devices Powered by Low Grade Heat - Krakow, B., Rahman, M.,
- Prototype and Simulation Model for a MEMS Magneto-caloric Refrigerator - Bhansali, S., Bhethanabotla, V., Rahman, M.

University of West Florida

- Software Agents and Knowledge Discovery and Data Mining for Enhanced Safety and Control of Hydrogen Operations - Bradshaw, J; Glymore, C; Bunch, L, Hanson, J.

A report for the first year's effort was completed by FSEC in November 2003 and sent to the NASA program managers at GRC and KSC. This 2003 report contained individual project activities for each of the funded projects.

During the initial year of the project, the NASA managers required periodic review meetings be held in order to appraise the projects goals, benefits to NASA and expected results. During the first year, two project review meetings were held, one on January 14-16, 2003 at the University of South Florida in Tampa and one on August 12-15, 2003 at the University of Florida in Gainesville. The project review meetings were to be held at all the participating universities and covered, in addition to project reviews, tours of the labs and facilities at the host university.

Each of the review meetings took 3 to 4 days due to the large number of project presentations. Each project presentation was given 20 minutes for the power point slides followed by a 10-minute question and answer period. Following all the presentations at each review meeting, FSEC program managers met with the five to six NASA reviewers that had attended the meeting to discuss individual projects. These discussions concerned the project's need, benefits and results and included recommended changes in the project direction and activity. Following the two first year review meetings, five projects were judged complete and six projects were added to the program. The added projects were either redirected projects from the first year or new efforts requested by NASA.

During the second year, the spring project review meetings were held on March 3-4, 2004 at Florida State University in Tallahassee and March 30-31, 2004 at the University of Central Florida in Orlando and the fall meeting on September 21-22, 2004 at the Florida Solar Energy Center in Cocoa.

A report for the activities at the end of year two was prepared for the NASA GRC program manager in November 2004. Following a NASA GRC management change, the November 2004 report was updated and sent to NASA GRC in June 2005. This report was named the project report for FY 2003 which then was published as NASA Contract Report #2006-214326. The projects covered in the NASA CR are given in Table 2.

Table 2. Projects published in NASA CR 2006-214326, June 2005.

Florida Solar Energy Center

- Analysis of Alternative Hydrogen Production Processes Liquid Hydrogen Production via Sub-Quality Natural Gases - Huang, C., T-Raissi, A.
- Characterization of Spin-Coated Terbium-Doped Strontium Cerate Thin Film Membranes - Elbaccouch, M., Mohajeri, N., T-Raissi, A.
- Development of Tribological Coatings for Cryocoolers - Dhere, D.
- Experimental Design and Evaluation of ZBO Cryogenic Systems - Baik, J.
- Hydrogen Education and Outreach – Schleith, S., Hall, P., Henzmann, A., Block, D.
- Hydrogen Production from Used Lube Oil via Supercritical Water Reformation - T-Raissi, A., Ramasamy, K.
- Hydrogen Production via Photocatalysis - Linkous, C., Bateman, C., Chan, Q.
- Hydrogen Purification and Storage Using Lithium Borohydride - Linkous, C.
- Hydrogen Storage and Recovery in Ammonia Borane Complex - T-Raissi, A., Mohajeri, N.
- Liquid Hydrogen Storage at Kennedy Space Center - Gu, L., Bokerman, G., T-Raissi, A.
- Local Hydrogen Production via Catalytic Reformation of Fossil and Renewable Feedstocks - Muradov, N., Smith, F.
- Photoelectrochemical Water Splitting for Hydrogen Production Using Multiple Bandgap Combination of Photovoltaic Cells and Photocatalyst. - Dhere, N.
- R & D Processes for Increasing the Fluid Density of Cryogenic Liquids - Baik, J.
- Smart Paints and Pigments for Hydrogen Sensing - Mohajeri, N., Bokerman, G., Muradov, N., T-Raissi, A.
- System Analysis of Hydrogen Production and Utilization at KSC - T-Raissi, A., Elbaccouch, M., Ramasamy, K.

University of Central Florida

- Development of Cryogenic Shape-Memory Actuator Materials for Switches, Seals and Valves - Vaidyanathan, R.
- High Selective Nano-MEMS Low Temperature Sensor - Seal, S., Shukla, S.
- Metal Hydrides for Hydrogen Separation, Recovery and Purification – Hampton, M., Slattery, D.
- Novel Technique for the Detection and Location of Hydrogen Leaks - Sellar, G.
- Reverse Turbo Brayton Cycle Cryocooler Development for Liquid Hydrogen Systems - Chow, L., Kapat, J., Chen, Q.

Florida State University

- Development of Optical Systems for Mass and Two Phase Flow Gauging – Van Sciver, S., Justak, J.
- Experimental and Numerical Investigations of Cryogenic Multiphase Flow - Van Sciver, S., Hussaini, Y.
- Measurement of Transport Properties of Densified LH_2 and LO_2 - Van Sciver, S., Celik, D., Hilton, D.

Florida International University

- Development and Demonstration of a Pilot-Scale Biomass Gasification Unit for Hydrogen Production - Srivastava, R., Mazumdar, A.

University of South Florida

- By Product Hydrogen Production - Stefanakos, E., Krakow, B., Moore, G., Wolan, J., Smith, M.
- Development of a Numerical Simulation Model for Thermo-Fluid Analysis and Design Optimization of Cryogenic Storage Systems with Zero Boiloff - Rahman, J., Ho, S.
- Development of Rectenna Solar Energy Conversion for Local Hydrogen Production - Buckle, K., Bhansali, S., Goswami, Y.
- Hydrogen Gas Sensors by Surface Acoustic Waves - Bhethanbotla, V., Joseph, B.
- Hydrogen Production via Methane Nonoxidative Aromation - Wolan, J., Kababji, A.
- Prototype and Simulation Model for a Magneto-Caloric Refrigerator - Bhansali, S., Bhethanabotla, V., Rahman, M.

University of West Florida

- Software Agents and Knowledge Discovery and Data Mining for Enhanced Safety and Control of Hydrogen Operations - Bunch, L.

Following the project review in September 2004, a decision was made by the FSEC and NASA project managers on continuation of the existing projects and the desire to add new activities. This led to issuance of a second RFP. This RFP allowed for submission of both continuing and for new projects. Following extensive FSEC and NASA review, six old projects were discontinued and six new ones were initiated. The new projects are given in Table 3.

Table 3. New projects began in January 2005

- Development of High Temperature Proton Exchange Membrane Electrolytes - Linkous, C (FSEC)
- Genetic Engineering of Escherichia Coli to Enhance Biological Hydrogen Production from Biomass-Derived Sugars - Self, W (UCF)
- Modeling and Optimization of Fuel Cell Systems for Aircraft Applications - Ordonez, J (FAMU)
- Smart Porous Metal-Organic Frameworks for Hydrogen Recovery and Storage - Eddaoudi, M (USF)
- Solar Powered Hydrogen Production via a High Temperature Photocatalytic Water Splitting Cycle - Huang, C (FSEC)
- Wireless Passive Sensors and Systems for Physical and Hydrogen Sensing Applications - Malocha, D (UCF)

With regard to yearly reports, a report for FY 2004/2005 was prepared and sent to NASA GRC in June 2006. The next program change occurred in September 2006 when the fourth and last funding increment was received from NASA GRC. At this time, the program was to place more emphasis on the development of fuel cells. The list of projects for the last phase of the program is given in Table 4. Table 4 also includes the final reports for four projects that were given in the FY 2004/2005 report. These projects were considered completed and, thus, are reported here. The projects listed in Table 4 are the ones presented in this report.

With regard to review meetings, the final two review meetings were held on May 11-15, 2005 at the University of Florida in Gainesville and on November 1-4, 2005 at the Florida Solar Energy Center in Cocoa.

Table 4. Project listing for the period of 2005 through 2007.

Florida Solar Energy Center

- Ammonia-Borane Complex for Hydrogen Storage - Mohajeri, N., T-Raissi, A., Ramasamy, K., Adebiyi, O., Bokerman, G.
- Ceramic Membranes of Mixed Ionic-Electronic Conductors for Hydrogen Separation - Elbaccouch, M., T-Raissi, A., Linkous, C., Mohajeri, N.
- Compact, Lightweight and Optimized Fuel cells for Space or Aircraft Power - Fenton, J, Choi, P., Bonville, L., Kunz, R.
- Gas Permeable Chemochromic Compositions for Hydrogen Sensing - Mohajeri, N., Muradov, M., Bokerman, G., T-Raissi, A., Captain, J., Peterson, B., Whitten, M.
- Hydrogen Education and Outreach – Schleith, S., Hall, P., Henzmann, A., Block, D.
- Hydrogen Production from Used Lube Oils - T-Raissi, A., Ramasamy, K.
- Hydrogen Production via Solar Thermochemical Water Splitting – T-Raissi, A., Huang, C., Muradov, N.
- Hydrogen-Powered Aeropropulsion: Compact, Lightweight and Efficient Fuel Cells for Space Power - Linkous, C., Pearman, B., Hall, D., Slattery, D., Baik, J.
- Integrated Fuel Cell Test Bed Facility - Slattery, D., Bonville, L., Fowler, R.
- Liquid Hydrogen Storage at Kennedy Space Center - Gu, L., Block, D., Bokerman, G., T-Raissi, A., Basarkar, M.
- Local Hydrogen Production via Catalytic Reformation of Fossil and Renewable Resources - Muradov, N., Smith, F.
- Photoelectrochemical Water Splitting for Hydrogen Production Using Multiple Bandgap Combination of Thin-Film- Photovoltaic Cells and Photocatalyst – Dhere, N.
- System Analysis of Hydrogen Production and Utilization at KSC - T-Raissi, A., Elbaccouch, M., Ramasamy, K., Baik, J.
- Zero-Boil-Off Liquid Hydrogen Storage Tanks - Baik, J.

University of Central Florida

- A Reliable, Efficient and Compact Reverse Turbo Brayton Cycle Cryocooler for Storage and Transport of Hydrogen in Spaceport and Space Vehicle Applications - Chow, L., Kapat, J., Chen, Q., An, L., Wu, T., Sundaram, K., Ham, C., Dhere, N.
- Development of Cryogenic Shape Memory Actuator Materials for Switches, Seals and Valves - Vaidyanathan, R.
- Genetic Engineering to Enhance Biological Hydrogen Production - Self, W., Ganyc, D., Halvorsen, L.
- Highly Selective Nano-Mems Low Temperature Hydrogen Sensor- Seal, S., Cho, H.
- Metal Hydrides for Hydrogen Separation, Recovery and Purification - Hampton, M., Slattery, D.
- Wireless Passive Sensors and Systems for Physical Sensors and Hydrogen Sensing Applications - Malocha, D.

Florida State University

- Densified LH_2 and LO_2: Transport Properties and Density - Van Sciver, S.

- Experimental and Numerical Investigations of Cryogenic Multiphase Flow - Van Sciver, S., Hussaini, Y., Justak, J.

Florida International University

- Improved Hydrogen Yield from Florida Specific Biomass Gasification Using a Pilot Scale Gasification Unit - Srivastava, R.

University of South Florida

- Numerical Simulation Model for Thermo-Fluid Analysis of Cryogenic Storage Systems with Zero Boiloff - Rahman, J., Ho, S.
- Prototype and Simulation Model for a Magneto-Caloric Refrigerator - Bhansali, S., Rahman, M., Kim, S., Ghirlanda, S., Hernandez, C., Adams, C., Bethala, B., Rosario, S., Sambandam, S.
- Smart Porous Metal-Organic Frameworks (MOFs) for Hydrogen Recovery and Storage - Eddaoudi, M., Zaworotko, M., Space, B., Eckert, J., T-Raissi, A., Mohajeri, N.
- Surface Acoustic Wave (SAW) Sensors for Hydrogen and Other Gas Detection - Bhethanabotla, V
- Thermo Catalytic H2 Production via Oxygen-Free Methane Aromatization - Wolan, J., Stefanakos, E., Kababji, A.

Florida A & M University

- Modeling and Optimization of Fuel Cell systems for Aircraft Applications - Ordonez, J., Lungo, C.

As previously mentioned, this program covered research in a broad area of hydrogen technologies. A brief description of the final projects presented by hydrogen technology areas are as follows:

Hydrogen Production – In Florida, NASA KSC and Cape Canaveral Air Force Station will eventually require local production facilities because of economics, transportation safety and quantity requirements. Thus, local hydrogen production was a major task of the program. Eight projects were carried out under this general heading:

- Genetic Engineering to Enhance Biological Hydrogen Production - Self, W., Ganyc, D., Halvorsen, L. (UCF)
- Hydrogen Production from Used Lube Oils - T-Raissi, A., Ramasamy, K. (FSEC)
- Hydrogen Production via Solar Thermochemical Water Splitting – T-Raissi, A., Huang, C., Muradov, N. (FSEC)
- Improved Hydrogen Yield from Florida Specific Biomass Gasification Using a Pilot Scale Gasification Unit - Srivastava, R. (FIU)
- Local Hydrogen Production via Catalytic Reformation of Fossil and Renewable Resources - Muradov, N., Smith, F. (FSEC)
- Photoelectrochemical Water Splitting for Hydrogen Production Using Multiple Bandgap Combination of Thin-Film Photovoltaic Cells and Photocatalyst – Dhere, N. (FSEC)
- System Analysis of Hydrogen Production and Utilization at KSC - T-Raissi, A., Elbaccouch, M., Ramasamy, K., Baik, J. (FSEC)
- Thermo Catalytic H_2 Production via Oxygen-Free Methane Aromatization - Wolan, J., Stefanakos, E., Kababji, A. (USF)

Fuel Cells – Fuel cells offer new aircraft power options that can meet NASA's vehicle requirements. Of the five types of fuel cells, proton exchange membrane (PEM) fuel cells are the leading candidate for next generation space and aircraft power due to their high specific power output. This task addressed several innovative PEM fuel cell technologies as follows:

- Compact, Lightweight and Optimized Fuel cells for Space or Aircraft Power - Fenton, J, Choi, P., Bonville, L., Kunz, R. (FSEC)
- Hydrogen-Powered Aeropropulsion: Compact, Lightweight and Efficient Fuel Cells for Space Power - Linkous, C., Pearman, B., Hall, D., Slattery, D., Baik, J. (FSEC)
- Integrated Fuel Cell Test Bed Facility - Slattery, D., Bonville, L., Fowler, R. (FSEC)
- Modeling and Optimization of Fuel Cell Systems for Aircraft Applications - Ordonez, J., Lungo, C (FAMU)

Hydrogen Sensors – Cost effective hydrogen sensor technologies that can deliver detection selectivity and sensitivity, dependability and durability, stability and reproducibility, and applicability in cryogenic LH_2 environment are needed. Projects conducted in this area were:

- Gas Permeable Chemochromic Compositions for Hydrogen Sensing - Mohajeri, N., Muradov, M., Bokerman, G., T-Raissi, A., Captain, J., Peterson, B., Whitten, M. (FSEC)
- Highly Selective Nano-Mems Low Temperature Hydrogen Sensor- Seal, S., Cho, H. (UCF)
- Surface Acoustic Wave (SAW) Sensors for Hydrogen and Other Gas Detection - Bhethanabotla, V. (USF)
- Wireless Passive Sensors and Systems for Physical Sensors and Hydrogen Sensing Applications - Malocha, D. (UCF)

Hydrogen Storage and Liquefaction – Use of hydrogen as an energy carrier and fuel for spaceport and vehicle applications requires that it be stored and transported. New and innovative technologies are needed for higher energy density and safe H_2 storage and transport. The storage and liquefaction projects were:

- A Reliable, Efficient and Compact Reverse Turbo Brayton Cycle Cryocooler for Storage and Transport of Hydrogen in Spaceport and Space Vehicle Applications - Chow, L., Kapat, J., Chen, Q., An, L., Wu, T., Sundaram, K., Ham, C., Dhere, N. (UCF)
- Ammonia-Borane Complex for Hydrogen Storage - Mohajeri, N., T-Raissi, A., Ramasamy, K., Adebiyi, O., Bokerman, G. (FSEC)
- Liquid Hydrogen Storage at Kennedy Space Center - Gu, L., Block, D., Bokerman, G., T-Raissi, A., Basarkar, M. (FSEC)
- Numerical Simulation Model for Thermo-Fluid Analysis of Cryogenic Storage Systems with Zero Boiloff - Rahman, J., Ho, S. (USF)
- Prototype and Simulation Model for a Magneto-Caloric Refrigerator - Bhansali, S., Rahman, M., Kim, S., Ghirlanda, S., Hernandez, C., Adams, C., Bethala, B., Rosario, S., Sambandam, S. (USF)
- Smart Porous Metal-Organic Frameworks (MOFs) for Hydrogen Recovery and Storage - Eddaoudi, M., Zaworotko, M., Space, B., Eckert, J., T-Raissi, A., Mohajeri, N. (USF/FSEC)
- Zero-Boil-Off Liquid Hydrogen Storage Tanks - Baik, J. (FSEC)

Cryogenics – NASA Glenn research engineers have been working in the field of high-energy, high-density cryogenic propellants for over two decades. This basic research area focused on

developing handling capabilities and defining and measuring low temperature performance characteristics of cryogenic propellants.

- Development of Cryogenic Shape Memory Actuator Materials for Switches, Seals and Valves - Vaidyanathan, R. (UCF)
- Densified LH_2 and LO_2: Transport Properties and Density - Van Sciver, S. (FSU)
- Experimental and Numerical Investigations of Cryogenic Multiphase Flow - Van Sciver, S., Hussaini, Y. (FSU); Justak, J. (ATG)

Hydrogen Separation – Hydrogen is lost by NASA operations due to transfer, boil off and purging. In addition, prior to filling lines with liquid hydrogen, they must be precooled with liquid helium and then the helium is purged. Recovery of this lost hydrogen and helium could lead to substantial savings and led to these two projects.

- Ceramic Membranes of Mixed Ionic-Electronic Conductors for Hydrogen Separation - Elbaccouch, M., T-Raissi, A., Linkous, C., Mohajeri, N. (FSEC)
- Metal Hydrides for Hydrogen Separation, Recovery and Purification - Hampton, M., Slattery, D. (UCF/FSEC)

Hydrogen Education and Outreach

- Hydrogen Education and Outreach – Schleith, S., Hall, P., Henzmann, A., Block, D. (FSEC)

With reference to the above projects, it is noted that the projects for each of the hydrogen technologies were reasonably split with eight projects in production and two projects in separation.

It is also noted that ten projects began in 2002 and continued until the program end in 2007. These ten projects are shown in Table 5.

Table 5 - Projects covered the full grant time period.

- A Reliable, Efficient and Compact Reverse Turbo Brayton Cycle Cryocooler for Storage and Transport of Hydrogen in Spaceport and Space Vehicle Applications - Chow, L., Kapat, J., Chen, Q., An, L., Wu, T., Sundaram, K., Ham, C., Dhere, N. (UCF)
- Densified LH_2 and LO_2: Transport Properties and Density - Van Sciver, S. (FSU)
- Development of Cryogenic Shape Memory Actuator Materials for Switches, Seals and Valves - Vaidyanathan, R. (UCF)
- Highly Selective Nano-Mems Low Temperature Hydrogen Sensor- Seal, S., Cho, H. (UCF)
- Hydrogen Education and Outreach – Schleith, S., Hall, P., Henzmann, A., Block, D. (FSEC)
- Local Hydrogen Production via Catalytic Reformation of Fossil and Renewable Resources - Muradov, N., Smith, F. (FSEC)
- Numerical Simulation Model for Thermo-Fluid Analysis of Cryogenic Storage Systems with Zero Boiloff - Rahman, J., Ho, S. (USF)

- Prototype and Simulation Model for a Magneto-Caloric Refrigerator - Bhansali, S., Rahman, M., Kim, S., Ghirlanda, S., Hernandez, C., Adams, C., Bethala, B., Rosario, S., Sambandam, S. (USF)
- Surface Acoustic Wave (SAW) Sensors for Hydrogen and Other Gas Detection - Bhethanabotla, V. (USF)
- System Analysis of Hydrogen Production and Utilization at KSC - T-Raissi, A., Elbaccouch, M., Ramasamy, K., Baik, J. (FSEC)

As a final comment on the projects that were conducted, it is noted that each of the university participants have made educational activities a major part of their research program. The educational component has used the research projects as part of graduate student masters and PhD theses and training. The FSEC program expanded the education effort to include K-12 education and public outreach activities. Table 6 presents the totals for publications, presentations and students trained for each institution by their program.

Table 6. Publications, presentations and student by institution.

Institution	Publications	Presentations	Students
Florida Solar Energy Center	93	78	13
University of Central Florida	71	72	35
Florida State University	15	11	2
Florida International University	-	-	-
University of South Florida	33	28	24
Florida Agricultural & Mechanical University	10	7	22
Totals	222	196	96

To conclude this section on projects, one-page summaries of each of the 29 projects followed by the individual final reports are presented in the last two sections of this report. Detailed information on each of the projects is also available at: http:// www.fsec.ucf.edu/ hydrogen/new/ research/funded_nasa.htm and http://www.hydrogenresearch.org.

Projects Funded by Other Agencies or Industry

In the previous section, a listing of the projects that were conducted under the NASA grant was presented. One of the significant outcomes of the NASA grant was the development of strong R&D programs by many of the program PIs at each of the universities. These researchers have developed novel hydrogen and hydrogen related technologies that have the potential to become topics of interest to other funding agencies or industry. This section of the report presents a listing of those projects which have received additional funding from other agencies or industry and in which the research is still being conducted under the new agency funding. It is noted that these projects are not an official part of the NASA grant, but they are related to the NASA effort

in that the NASA program initiated the effort which is now receiving additional support. For this area, there are twelve projects presented in Table 7.

Table 7. Related projects funded by other agencies/industries.

Project Title	Funding Amount	University	Funding Agency	Comments
Thermochemical Conversion of Biomass to Liquid Hydrocarbons as Substitutes for Petroleum-based Fuels	$998,000	FSEC	FL DACS/ FHI/DOE/ Chevron/EES	F-T conversion of biomass to diesel fuel
Smart Paints for Hydrogen Leaks	No funding	FSEC	NASA-KSC	Tape being tested for use on shuttle launch site.
Smart Paint Pigments for Hydrogen Sensing	$375,000	FSEC	U.S. Navy	Smart paints used for rapid testing storage materials.
Hydrogen Production by Solar Thermochemcial Water-Splitting Cycles	$2,500,000	FSEC	SAIC/U.S. DOE	Solar hydrogen production. Total DOE funding of $4.5 million over 4 years.
Nanocrystalline Al-Mg Alloys for Hydrogen Storage	$300,000	UF/FSEC	NSF	Fabricate nanocrystalline magnesium alloys for hydrogen storage.
Lunar Hydrogen - Metal Hydride System	$71,735	FSEC	ASRC/NASA-KSC	Design and test metal hydride systems for lunar mission.
Metal-Organic Frameworks for High Capacity Hydrogen Storage	$280,000	USF/FSEC	U.S. DOE	Develop MOFs for high capacity hydrogen storage.
On-site Reformation of Diesel Fuel for Hydrogen Fueling Station Applications	$500,000	FSEC	Chevron/FHI/U.S. DOE	Reform diesel fuel to hydrogen.
Hydrogen Sensor with High Selectivity and Sensitivity at Room Temperature	$102,000	UCF	NSF	Hydrogen sensing.
Nano-particles/tubes Integrated MEMS Device for Point Contact Highly Sensitive Hydrogen Sensor	$174,000	UCF	ASRC/NASA-KSC	Hydrogen sensing.
Technology Demonstration of a 100 KW Biomass Gasifier in El Salvador	$1,026,000	FIU	DOD	Hydrogen production in El Salvador.

GIS Assessment of Florida Biomass Resources for Local Energy Production	$9,500	FIU	FL DEP/FSEC	Biomass resource in Florida.
TOTAL ADDITIONAL FUNDING:	**$6,336,285**			

1. Thermochemical Conversion of Biomass to Liquid Hydrocarbons as Substitutes for Petroleum-based Fuels – The goal of this project is to further develop and demonstrate a process for generating clean-burning synthetic liquid hydrocarbon fuels made from Florida biomass resources as well as the large quantities of animal wastes available throughout the State. In this project, biomass feedstock will be gasified to form a bio-syngas suitable for reformation via Fischer Tropsch (F-T) synthesis to form synthetic liquid fuels, e.g., bio-gasoline and/or diesel. Both the gasification and F-T technology are well established industrial processes but mostly used for coal or natural gas conversion. In this project we intend to further develop and demonstrate the technology for converting biomass feedstock and various animal wastes to gasoline and diesel range fuels. This activity has been funded by the Florida Department of Agriculture and Consumer Services, Chevron Corp. and Environmental Energy Systems, Inc. of Hialeah, FL

2. Smart Paints for Hydrogen Leaks – Monitoring hydrogen at the storage and usage sites for leakage is an important safety issue. FSEC has developed and filed for a U. S. patent on several formulations that act as smart paints for sensing hydrogen gas. Smart paints reveal, in an easy-to-see manner, the location of minute hydrogen leaks from pipes, flange joints, etc.

The dark spot on the "smart tape" indicates the location of hydrogen leak around this flange.

A roll of NASA-KSC fabricated "smart tape".

The “smart paint” in the form of a tape can be applied at the pipe connections, valve joints, or other areas susceptible to leaking. FSEC developed pigments that have been field tested at NASA-KSC for well over a year. And, NASA KSC has also applied for a patent under this project.

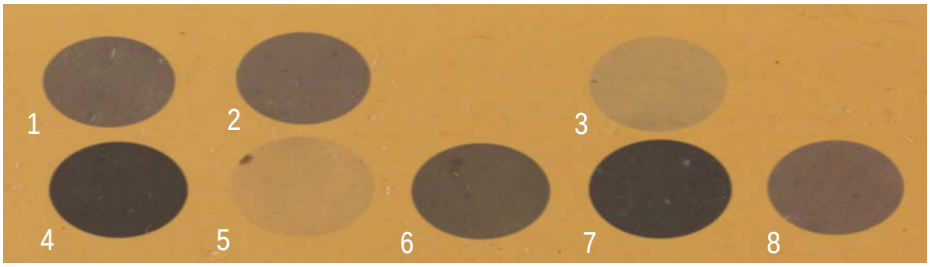
FSEC researchers have also developed special tungsten-based pigments that revert to the original color after exposure to hydrogen has ceased. These special reversible pigments

intended for “repeated use” applications, and they are also currently undergoing field-testing at NASA-KSC. KSC personnel have informed FSEC that KSC is planning in the near future to use the smart paint tape on the liquid hydrogen lines flowing from the storage tanks to the shuttle.

3. Smart Paint Pigments for Hydrogen Sensing – For a ‘hydrogen economy’, one of the major technology issues yet to be addressed involves its safe storage. If hydrogen can be stored safely and efficiently, it will open up many potential applications for its use. There are many potential candidate materials that can store hydrogen and identifying prospective candidates require a rapid and efficient material screening process.

FSEC researchers will design, fabricate, and test a high throughput-screening system based on the FSEC-developed hydrogen sensing polymers. The technique is applicable to a broad range of absorbents, including metal-organic frameworks (MOFs), various doped and undoped hydrides (e.g. alanates, alanes, etc.), among others.

FSEC’s hydrogen sensing membranes allow simple visual inspection of the chemochromic membranes after each dehydriding test. The change in the color of the membrane directly depicts the amount of hydrogen release from the samples. Under a new contract from the U.S. Navy, Defense Logistics Agency, FSEC researchers will be developing an apparatus and methods for high throughput combinatorial testing of hydrogen storage materials. The FSEC-developed technique reduces the time now required for screening for hydrogen storage materials from days down to a few minutes. The Navy funding for this project is $375,000.



A 25-mil thick section of FSEC-developed chemochromic film after exposure to various quantities of hydrogen gas.

4. *Hydrogen Production by Solar Thermochemical Water-Splitting Cycles –* Past research in solar thermochemical cycles has focused on processes that utilize only the thermal component of the solar spectrum. FSEC’s approach employs the high-energy photons within the solar spectrum to drive ammonium sulfite/ammonium sulfate redox system for photocatalytic production of hydrogen from water. Thus, the cycle uses both the photonic and thermal energies. FSEC developed water splitting cycle has received the Innovative Technology Award at the 15th World Hydrogen Energy Conference held in Yokohama Japan in 2006 – the only such award given to researchers from the U.S.A. A patent on the cycle has been filed. For this project, FSEC partnered with the Science Applications International Corporation of San Diego, CA. The U.S. DOE funding to FSEC for this project is $2.0 million plus cost share for the first year beginning August 2007. The total project effort is $4.5 million over four years.

Photoreactor for high temperature solar powered hydrogen production.

5. ***Nanocrystalline Al-Mg Alloys for Hydrogen Storage –*** The objectives of this effort are to fabricate nanocrystalline magnesium alloys (Al-Mg) in the form of powder via electrodeposition, characterize the microstructural evolution during hydrogenation and dehydrogenation, and then design an alloy powder with optimized characteristics. FSEC researchers have looked at alanates in the past. However, this new work involves nanocrystalline materials – materials with very tiny particles with a shorter path for the hydrogen, giving them a faster dehydriding rate. FSEC in a joint effort with the University of Florida investigating the use of metal hydrides for hydrogen storage. The project is funded by NSF at $300,000.

6. ***Lunar Hydrogen - Metal Hydride System –*** In 2005, NASA initiated the Regolith and Environment Science & Oxygen and Lunar Volatiles Extraction (RESOLVE) project to develop hardware under the NASA Exploration Technology Development Program (ETDP). The RESOLVE objective is to quantify volatiles released from lunar regolith (soils) and demonstrate in-situ resource utilization (ISRU) on a small scale by capturing the water and hydrogen volatiles. A metal hydride system has been initially designed for use in the system. However a more suitable metal hydride is needed because the current system does not work well at the desired temperatures. FSEC was tasked to identify a metal hydride based system that will capture hydrogen from a mixed gas stream and release the hydrogen when needed (a reversible system). The system captures 1.0 g of hydrogen in every cycle and is able to cycle 50 times. Ideally the system will absorb near room temperature, but absorption temperatures between 20-120^{o}C with desorption temperatures lower than 300^{o}C are desirable. FSEC has been funded by Arctic Slope Research Corp. at NASA-KSC for the amount of $71,735.

7. ***Metal-Organic Frameworks for High Capacity Hydrogen Storage –*** Metal-organic frameworks (MOFs) are a new class of metal-organic materials that exhibit desirable properties akin to zeolites, but also allow for tenability (pore size, organic functionality, choice of metallic constituents, inclusion of polar/ionic character) and rational design of desirable storage properties. These factors make MOFs a promising candidate for use as high capacity hydrogen storage materials. This project is concerned with developing and understanding new pathways aimed at synthesizing MOFs. The design strategy involves choosing the desired building blocks for the assembly step in a “top-down design” process, followed by directed assembly, “bottom-up synthesis”. This project is a cooperative effort between Dr. M. Eddauodi of USF and FSEC. It is funded by the U.S. Department of Energy, Basic Energy Sciences, at $280,000 for three years.

8. ***On-site Reformation of Diesel Fuel for Hydrogen Fueling Station Applications –*** The objectives of this project are to develop a cost effective, energy efficient and near-term on-site fuel reformation process for producing hydrogen (particularly high purity H_2) from sulfurous liquid hydrocarbon fuels (e.g. diesel, kerosene and/or jet fuels). Once developed, the process will be used at the hydrogen fueling stations and for applications that involve remote fuel cell based electric power generation in areas without access to natural gas or grid power. This activity is a collaborative RD&D effort between FSEC and the Catalysis Group at Chevron Technology Ventures, LLC. The project is funded by the U.S. Department of Energy through the Florida Hydrogen Initiative at $500,000 with $200,000 in cost share from Chevron Corp. and UCF.

9. ***Hydrogen Sensor with High Selectivity and Sensitivity at Room Temperature –*** This University of Central Florida project is developing and studying the defect structure of oxides at the nano-level for the development of high performance hydrogen sensors. The project will also investigate the selectivity issues by using ceramic separation membranes and the effect of UV exposure on sensor cleaning is further investigated. The study will ascertain the underlying mechanism for exhibiting enhanced sensor response of doped oxide nanoparticles and nano-wires at room temperature. This aspect would be a significant step towards room temperature H_2 sensor. Funded by NSF for $102,000.

10. ***Nano-particles/tubes Integrated MEMS Device for Point Contact Highly Sensitive Hydrogen Sensor –*** The advanced concepts in H_2 separation and gas sensing technologies are merged for the development of a novel H_2 sensor consisting of porous, doped, nano-clustered particulate/fiber/rod shaped nanostructures. Additionally, the sensor will be a unique integration of nanomaterials and MEMS device, thus combining the faculty expertise from UCF's materials, nanoscience, and MEMS fabrication technology. Funded by ASRC Corp. at NASA KSC for $174,000.

11. ***Technology Demonstration of a 100 KW Biomass Gasifier in El Salvador –*** Florida International University (FIU) is assisting the U.S. Department of Defense (DOD) to facilitate the exchange of information and technology with western hemisphere nations under the auspices of the Western Hemisphere Information exchange (WHIX) program. An element of the WHIX program is the technology demonstration and validation of innovative technologies that further the efficient management of military installations and protect the environment while ensuring safety and occupational health of workers and residents. FIU has installed and operated a 100 KW biomass gasifier (wood chips) for the U.S. military base in El Salvador for a period of 6 months. Funded by the U.S. Department of Defense for $1,026,000.

12. ***GIS Assessment of Florida Biomass Resources for Local Energy Production –*** The Florida Energy Office (FEO) was tasked with mapping of the state's potential biomass resources with the ultimate goal of prioritizing future development of resources and related technologies that will lead to a Florida bio-based economy. The Florida Solar Energy Center (FSEC) and the Applied Research Center at Florida International University assisted FEO with the creation of a statewide computer based compendium of biomass resource maps along with installed and potential biomass energy production capacity. GIS technology was used to create a portfolio of biomass resource maps and to identify installed and potential biomass energy production capacity statewide. Funded by Florida Department of Environmental Protection for $9,500.

The total external funding for the above twelve projects is **$6.336 million**.

Concluding Remarks

The NASA Hydrogen Research at Florida Universities program has demonstrated that six Florida universities within the State University System all working collaboratively can successfully address a major problem of national interest, hydrogen economy. Each of the partner universities has identified areas of expertise and interest while contributing to the overall success of the program. This final report has described the R&D activities and projects conducted for NASA under the five-year NASA Hydrogen Research at Florida Universities grant program. The R&D activities cover hydrogen technologies related to production, cryogenics, sensors, storage, separation processes, fuel cells, resource assessments and education.

In the span of six years, the NASA Hydrogen Research at Florida Universities program funded a total of 44 individual university projects, and employed more than 100 faculty and over 100 graduate research students at the six participating universities. Program researchers have filed more than 20 patents in all hydrogen technology areas and put out well over 220 technical publications in the last two years alone. The NASA research grant has also led to the universities receiving over $6.336 million of additional funding from federal agencies for research on twelve projects - all related to the NASA funded effort.

Finally, it is noted that each of the university participants have made educational activities a major part of their research program. The educational component has used the research projects as part of graduate student masters and PhD theses and training. The numbers of students trained by this research were 15 PhD, 23 M.S., 2 post doctorial, 20 undergraduate and 36 unknown for a total of 96 students. The FSEC program expanded the education effort to include K-12 education and public outreach activities.

In the next two sections are one-page summaries of each of the 29 projects followed by the individual final reports. The reports are organized individually from each of the universities and presented in alphabetical order of the project title. These one-page summaries and the following complete reports are presented in the same order as the listing of reports given in Table 4. The complete name, title and affiliation of each project principal investigator are given in Appendix A.

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