

Ammonia-Borane Complex for Hydrogen Storage

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Research Period: June 2002 to December 2007

Summary

The goal of this project was to develop a high-density hydrogen storage system based on ammonia borane (AB) complex. Due to their high hydrogen capacity, AB hydrides have been employed as disposable hydrogen (H_2) sources for fuel cell applications. The objectives of this project were to 1) identify viable amine-borane (AB) complexes for hydrogen storage at ambient conditions, and 2) develop a cost-effective synthetic route for hydrogenation of borazine to cyclotriborazane - as a means of chemical hydrogen storage.

Ammonia borane (AB) complex is a chemical hydride that is stable in air and water, and contains very high hydrogen content (19.6 wt%) with a system-level H_2 energy storage density of about 2.74 kWh/L (vs. 2.36 kWh/L for a liquid hydrogen Dewar). AB is a promising material as a hydrogen carrier especially for power generation utilizing proton exchange membrane fuel cells (PEMFC). Release of hydrogen in the AB complex can occur by either thermolysis or hydrolysis. Thermolysis of AB generates, in addition to hydrogen, species such as borazine, monomeric aminoborane, and diborane. In the case of AB hydrolysis, ammonia is the byproduct of the reaction.

The results have shown the liberation of 2 moles of hydrogen by thermolysis of AB complex with relatively minor expenditure of energy. Without downstream treatment, some quantities of borazine and poly-aminoborane are also generated. The results have also shown that borazine generated can be effectively captured and removed from H_2 gas stream using a broad class of solid sorbents including carbons and mesoporous silica.

Results for pyrolysis of the AB complex have shown it to be an overall exothermic process that requires induction energy to initiate AB decomposition until about 0.3 moles of H_2 is released. At this point, the reaction is self sustaining and proceeds to completion with the additional release of 2 moles of hydrogen gas. Induction energy required to release 2 moles of H_2 is about 16.2 kJ/mol of AB or 8.1 kJ/mol of H_2 , which corresponds to 3.35% of the chemical energy of hydrogen generated (on LHV basis).

Near room temperature hydrolysis of AB complex has been carried out using small amounts of K_2PtCl_6 salt. The AB hydrolytic reaction is exothermic and can be extremely fast, kinetically. The report also measures the thermal conductivities of composites formed by mixing fine aluminum powder with AB complex at temperatures in the range of 300-420K. At 300 K, the thermal conductivity of pure AB is approximately 15 W/m-K. A composite pellet prepared by mixing 10% by weight aluminum powder with AB complex had a thermal conductivity that was a factor of 4 higher than that of pure AB.

The research has resulted in one patent, 9 publications and 7 presentations.

Ceramic Membranes of Mixed Ionic-Electronic Conductors for Hydrogen Separation

PI: M. Elbaccouch, A. T-Raissi, C. Linkous, N. Mohajeri
(Florida Solar Energy Center)

Research Period: April 2004 to September 2007

Summary

Mixed ionic-electronic conductors of perovskite-type structure ($A^{2+}B^{4+}O_3$) are of interest for hydrogen production and separation at high temperatures. The goal of this project was to develop ion transport separation and purification systems using mixed ionic-electronic conductors of perovskite-type structure ($A^{2+}B^{4+}O_3$ -doped with a trivalent cation). The targeted membranes separate hydrogen from gas mixtures with 100% selectivity, high hydrogen flux, and good chemical stability in CO_2 -rich mixture. The designed membranes are dense and free of pinholes. For the project, three tasks were conducted as follows.

Task 1 - Hydrogen Flux in Terbium (Tb) Doped Strontium Cerate ($SrCeO_3$) Disk Membranes. In task 1, hydrogen membranes of $SeCe_{0.95}Tb_{0.05}O_{3-\delta}$ were synthesized using the liquid-phase method, and hydrogen flux data was generated under different processing conditions. The results evaluated hydrogen permeability as a function of temperature, hydrogen partial pressure, hydrogen dry conditions, and water vapor pressure. Also, the influence of nickel deposition on hydrogen flux was evaluated.

Task 2 - Microstructural Analysis of Doped-Strontium Cerate Thin Film Membranes Fabricated via Polymer Precursor Techniques. This task synthesized nanocrystalline thin film membranes of terbium (Tb)-doped strontium cerate ($SrCeO_3$) via the polymer precursor techniques. Continuous and dense thin film membranes of composition $SrCe_{0.95}Tb_{0.05}O_{3-\delta}$ were prepared using spin-coating technique by utilizing ethylene glycol (EG)-based polymeric precursor. The polymeric precursor was deposited on silicon-based substrates, and converted to dense polycrystalline thin film ceramic membranes by sintering at relatively low temperatures. The study demonstrated that using the EG-based polymeric precursor, Tb-doped $SrCeO_3$ thin film membranes, having thicknesses in the range of 0.2-2 μm and average nanocrystallite size of 8-70 nm, can be effectively synthesized by controlling the number of spin-coating cycles and sintering temperature.

Task 3 -Development of Ceramic Oxide Thin Films Using Tape-Casting Process. This task fabricated a tubular membrane reactor that could be used at temperatures (above 550 $^{\circ}C$) for hydrogen separation and purification. The tubular reactor was a mixed ionic-electronic conductive system with a doped perovskite structure ($A^{2+}B^{4+}O_3$ -doped with a trivalent cation). The reactor consists of a porous $SrCeO_3$ -NiO composite support and a dense thin film membrane of $SrCe_{0.95}Y_{0.05}O_{3-\alpha}$. The support material, composed of the ceramic powder, binder, plasticizer, and solvent, was formulated into homogeneously dispersed slurry with uniform structure. A tape-casting process was used to produce thin film support tapes. After drying, the tapes were cut and rolled on a rod producing a tubular geometry. Slow sintering and H_2 atmosphere exposure burned off the organic materials, producing a ceramic composite tube with appreciable porosity. From this work, 5 publications have resulted.

Compact, Lightweight, and Optimized Fuel Cells for Space and Aircraft Power

PIs: J. Fenton, P. Choi, L. Bonville, R. Kunz (Florida Solar Energy Center)

Research Period: June 2005 to February 2008

Summary

Proton exchange membrane (PEM) fuel cells are potentially the most efficient energy conversion devices for space applications. Conventional PEM fuel cells use external humidification requiring cumbersome humidification devices, which increase the volume and complexity of the fuel cell system. The research objective of this project was to achieve efficient fuel cell operation without external humidification of reactant gases by developing highly efficient and compact fuel cell systems which include efficient membrane electrode assemblies and internal water management systems.

To accomplish the objective, techniques were developed for improving PEM fuel cell performance when operating on dry reactants that are known to harm performance. The use of reactant recirculation, water recirculation, and a cell with membrane additives were considered. For reactant recirculation, a simple mass balance model was used to determine the membrane inlet relative humidity (RH) for a fuel cell operating on dry reactant gases. Calculations were done to vary cell temperature, cell pressure, reactant stoichiometry and reactant recycle in order to generate strategies for internally humidifying the stack and for operation under conditions which maximize power density. These calculations showed the cathode recycle was much more effective than the anode recycle at increasing the membrane inlet relative humidity. They also showed that for reasonable total flow rates, the losses due to reduced reactant pressures were much higher than the gains for the increased membrane water content.

A simplified and compact fuel cell system with no external humidification was designed and operated. A model was developed for the system, which includes a combined analysis of the generation of water in the fuel cell and the diffusion of water from the wet side of humidifier to the dry feed stream. Single cell and stack experiments of the internal humidifier incorporated cell have shown improved performance of fuel cell compared to the dry feed operation. However, the performance was lower than that of externally humidified operation by 20-30 % in a single cell experiment. Polymer membranes such as Nafion[®] and SPEEK have been successfully employed in the fuel cell system to provide the diffusion medium for the transport of water vapor from the humid exhaust gas to the dry feed stream. In order to improve the efficiency of the MEA, new composite membranes using inorganic acid were prepared and tested. The composite membrane showed higher performance, which may be attributed to the improved conductivity and lower ohmic resistance of the membrane.

The humidifier may be further improved by increasing the active area of diffusion and reducing the thickness of the membrane. The implementation of an internal humidifier with highly efficient MEAs provides the basis for a new compact fuel cell system for space applications.

The research has resulted in research for two graduate students, in one patent, in one publication and in two presentations.

Gas Permeable Chemochromic Compositions for Hydrogen Sensing

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Research Period: January 2004 to December 2007

Summary

The goal of this project was to develop a special powder material that can be applied like paint to the surfaces of cross-county lines at NASA-KSC and used for detecting hydrogen leaks. Operations at KSC require safety and the use of extremely pure hydrogen. The proposed technique provides a visual method to detect and locate possible hydrogen leaks that may occur in the field lines, flanges and joints for hydrogen transport and use. To detect the location of hydrogen leaks, a special chemochromic hydrogen (H₂) sensing material, called smart paint, has been researched, developed and patented by the Florida Solar Energy Center. The development of the smart paint sensors has also been done with close coordination and collaboration with scientists from NASA Kennedy Space Center.

The hydrogen (H₂) sensors are comprised of a gas permeable matrix material intermixed and encapsulating with at least one chemochromic pigment. The chemochromic pigment produces a detectable change in color of the overall sensor composition in the presence of H₂ gas. The hydrogen leaks are shown by changes in color from white to gray of the sensing material. Two types of sensors have been developed and field tested – one in which the color change is irreversible and one, called reversible, in which the changed color in the presence of H₂ is reversed to the original color when no H₂ is present.

The irreversible sensing material employs titania (TiO₂) supported palladium oxide (PdO) pigments encapsulated within a special silicone matrix. The results for the irreversible sensors determined the hydrogen activity of four different chemochromic TiO₂ supported PdO pigments, the chemochromic activity of the pigments as a function of the PdO particle size and level of PdO dispersion on the TiO₂ support surface and the materials kinetics and color contrast number.

The reversible H₂ sensors were formulated based on isopolycompounds (IPC) of tungsten and molybdenum, heteropolycompounds, HPC, all of which were synthesized and evaluated. For this case, results were determined for reversing enhancing agents polyoxometalates (POM) of W and Mo including silico-tungstic acid (STA) H₄[SiW₁₂O₄₀], phospho-tungstic acid (PTA) H₃[P(W₃O₁₀)₄], and phospho-molybdic acid (PMA) H₃[P(Mo₃O₁₀)₄]. POMs were doped with small amounts of Pt to catalyze the coloration-bleaching reactions. Two modifications of the reversible pigment were studied: (1) alumina-supported Pt-POM encapsulated in silicone matrix, and (2) Pt-POM supported on porous supports such as glass and paper filters. Both systems performed well during coloration and bleaching stages.

The research has resulted in one patent, one publication and two presentations.

Hydrogen Education and Outreach

PIs: S. Schleith, P. Hall, A. Henzmann, D. Block (Florida Solar Energy Center)

Research Period: June 2002 to December 2007

Summary

Education and outreach were extremely important components of the NASA hydrogen research program. These activities have supported four main areas: education of graduate and undergraduate engineering and science students, education for K-12 students and teacher professional development, participation in and offering of seminars and workshops, and a variety of public outreach activities.

Each of the university participants have made educational activities a major part of their research program. The universities have used the topics from the large variety of research projects for graduate student masters and PhD theses. In addition, the project's results are used for publications and presentations by university faculty members and their students to present the results to local, national and international audiences. The totals are 222 publications, 196 presentations and the support of 96 students.

The goal of incorporating hydrogen education into K-12 student and teacher programs at FSEC has been successfully accomplished through curriculum development, professional development for teachers and special events for K-12 students. These activities are ongoing and are being continually expanded. Over the course of the grant period, an average 310 teachers per year have participated in hydrogen education training opportunities facilitated by FSEC staff. The teacher opportunities include multi-day institutes, one-day workshops, and half-day experiences. Interest in hydrogen continues to grow amongst teachers, as evidenced by the popularity of the many hydrogen training events held for teachers by FSEC throughout the year. Field trips to the Florida Solar Energy Center are also popular with schools with nearly 800 students, their teachers and 60 parents per year visiting the facility for informal instruction on hydrogen, solar and energy efficiency.

Another major effort directed at graduate students and the technical community was the fuel cell short courses developed and offered for the past three years at the Florida Solar Energy Center. The courses are open to industry, academia and students and have drawn researchers and engineers from such places as NASA, UTC, Giner Electrochemical, Lawrence Berkeley National Lab, and Savannah River National Lab. Most attendees were from the US but some came from as far away as Spain and Japan.

The outreach program has been accomplished publications, presentations, press releases and web site development, as well as personal interaction with the public. Outreach results in addition to publications and presentations include 21 press releases and the development of two hydrogen web sites.

Hydrogen Production from Used Lubricating Oils

PIs: A. T-Raissi, K. Ramasamy (Florida Solar Energy Center)

Research Period: June 2005 to December 2007

Summary

Used lubricating oils present a valuable, readily available and cost-effective resource for local production of hydrogen at NASA-KSC. In Florida, the amount of used lubricating oil available for hydrogen production amounts to 45 million gallons per year at a relatively low cost of about 10 cents/gallon delivered. Used lube oils are a complex mixture of aliphatic and polycyclic hydrocarbons formulated to withstand high service temperatures in internal combustion engines. Both synthetic and mineral oils contain a high concentration of hydrogen (about 13–14 wt %). In this project, a process has been developed that converts used oils to hydrogen and other valuable low molecular weight hydrocarbons. The processes used were supercritical water reformation and steam pyrolysis.

The results show that hydrogen production from used lube oil via thermal cracking can be an attractive process both environmentally and economically. The performance of several dehydrogenation catalysts -- nickel, carbon, and an alkali based catalysts -- were investigated. Both nickel and carbon based catalysts performed poorly toward hydrogen production during steam assisted reformation of lube oils because of catalyst deactivation. Utilizing KOH as a catalyst for the reformation of lube oils increased the total yield of all the gaseous species produced with no noticeable degradation of the catalyst activity and with high selectivity toward hydrogen. However, the hydrogen yields were low.

Total gas produced and the yield of hydrogen were significantly higher during both steam assisted reformation and direct thermal cracking of the lube oils at 1 atm and reformer temperatures above 715°C as compared with those obtained by supercritical water reformation (65% of hydrogen contained in oil, compared with only about 5% from supercritical water reformation). The high temperature, low pressure process also yielded lower concentrations of CO₂ and CO in the output gas (30% compared with only 1% by volume of gas produced by supercritical water reformation).

Results obtained from the direct thermolytic reformation of the virgin synthetic (Mobile One™) oil and used oil showed that, respectively, 58–65% and 40–63% of the total mass of hydrogen in the oil fed into the reformer was converted to H₂ in the output gas. Composition of the gaseous species generated by thermal cracking and steam reformation of lube oils were basically the same and included mainly hydrogen, methane and ethylene at 17–30%, 40–45% and 15–25%, respectively. Under the experimental conditions of this investigation, the presence of water does not appear to affect the chemistry of the thermolysis of lube oils and only acts as a heat transfer medium. Direct thermolysis of lube oils requires less energy and produces about one third less disposable waste materials (compared to that from steam reformation process).

The research has resulted in six publications and two presentations.

Hydrogen Production via Solar Thermochemical Water Splitting

PIs: A. T-Raissi, C. Huang, N. Muradov (Florida Solar Energy Center)

Research Period: March 2004 to February 2008

Summary

One of the NASA objectives was to identify, characterize, and analyze a series of eco-friendly technologies that could be used for hydrogen production at NASA Kennedy Space Center (NASA-KSC) from locally available feedstock. One approach for hydrogen production that utilizes both local and renewable resources is splitting water using solar energy as the primary energy input. Technologies described in this project employ solar-driven thermochemical cycles for the direct (*i.e.* no intermediate electricity generation step is involved) production of hydrogen from solar energy and water. Any thermochemical water splitting cycle consists of two main steps: hydrogen and oxygen production steps. In this report, a new sulfur-family solar thermochemical water splitting cycle is described that utilizes the photonic portion of the solar spectrum for the production of hydrogen and the thermal part of the sunlight for the oxygen generation.

All sulfur-family thermochemical water splitting cycles rely on concentration and decomposition of sulfuric acid for the oxygen evolution step of the cycle. The sulfuric acid decomposition step presents serious materials and catalyst deactivation challenges. Thus, a new family of hybrid photo/thermo-chemical water splitting cycles based on a sulfur ammonia cycle has been developed.

Experimental results for the sulfur ammonia cycle show that the hydrogen generation step attains an efficiency of about 12% using precious metal doped cadmium sulfide photocatalyst. Due to the materials challenges of the sulfuric acid decomposition process, two new classes of cycles have been developed by modifying the original sulfur ammonia cycle to include 12 metal sulfate-ammonia ($M\text{SO}_4\text{-NH}_3$); and 3 metal pyrosulfate-ammonia ($M_2\text{S}_2\text{O}_7\text{-NH}_3$) based cycles. Experiments involving the zinc oxide catalyzed decomposition of ammonium sulfate using a thermogravimetric/ differential thermal analysis system couple to a mass spectrometer have shown the evolution of ammonia validating the feasibility of oxygen production via metal sulfate sub-cycles.

From this funded work, two patents, 8 publications and 8 presentations have resulted, and one post-doctoral and two graduate research students have been trained. This activity helped FSEC researchers secure a U.S. Department of Energy funding for \$4.5 million (2007-2011) for a project entitled "Solar High-Temperature Water-Splitting Cycle with Quantum Boost." This DOE awarded effort is a 50%-50% joint FSEC/Science Application International Corp. (SAIC) R&D program.

Hydrogen-Powered Aeropropulsion: Compact, Lightweight and Efficient Fuel Cells for Space Power

PI: C. Linkous, B. Pearman, D. Hall, D. Slattery, J. Baik
(Florida Solar Energy Center)

Research Period: September 2004 to December 2007

Summary

Fuel cells have long been used in supplying space power, however, improvements are still required in terms of size, weight, and fuel efficiency. In this project, various strategies for increasing the specific power (kilowatts of power per kilogram of device weight) of fuel cells were studied. The major objective was to increase the state-of-the-art fuel cell power density from ~100 W/kg to 1.0 kW/kg and higher.

The approach to improving power density was to increase the current density. Current density is frequently limited by electrolyte conductivity, especially for solid electrolytes. Thus, the research targeted the ionic conductivity of the electrolyte as a significant barrier in the development of higher power density devices. The effect of temperature was clearly demonstrated, with conductivity values rising on order of 4x in going from room temperature to 100 oC. Another strong effect was the acid electrolyte concentration where additional improvements in conductivity by >30% are gained by lowering concentration of the acid from its maximum value to the 4-6 M range. The combined effects can potentially produce a conductivity greater than 5x of the ambient concentrated acid value.

Liquid electrolytes must be contained in a porous matrix. Hexagonal boron nitride, h-BN, was a strong contender in this regard, due to its chemical inertness and fine particle size. Conductivities as high 0.25 S/cm with a phosphoric acid/BN paste were obtained, some 2.5 times that obtained with conventional solid polymer electrolytes. Boron carbide, BC, and silicon nitride, SiN, gave comparable results.

The research also showed the use of FLUENT® computer program as a performance modeling tool and investigated the pros and cons of the use of microphotography, solvent permeation, and conductivity of solvent extract for monitoring oxidative resistance to peroxide attack on polymer membranes. It was determined that the conductivity of the peroxide soaking solution itself was the best way of comparing rates of membrane degradation among many disparate ionomer materials. Another way to improve the conductivity of a proton-conducting electrolyte was to increase the acidity of the acid groups or molecules contained within it. In this later case, the research found that the sulfonic acid derivative of a polyaryletherketone known as SPEEK (polyetheretherketone sulfonate) was not a strong acid. It was attempted to prepare the superacidic α,α -difluoromethanesulfonic acid of SPEEK, starting with monobromination of 2,5-diacetamido-trifluoromethylbenzene. Finding a solvent that would dissolve both the trisubstituted benzene and the BBr₃ brominating agent and remain inert throughout the reaction proved to be a challenge.

The research resulted in 2 publications, 6 presentations and support of one visiting graduate student.

Integrated Fuel Cell Test Bed Facility

PIs: D. Slattery, L. Bonville, R. Fowler (Florida Solar Energy Center)

Research Period: January 2005 to December 2007

Summary

The goal of the Integrated Fuel Cell Test Bed (IFCT) facility was to create a proving ground and permanent test facility where fuel cell components and systems could be tested and their performance evaluated. The fully integrated test bed facility could also be used for determining figures of merit and performance metrics to include round trip efficiency, specific power (kW/kg), reliability for long duration operation (approximately 1 year), redundancy path development, waste heat/cooling/heating management, turn down effects, transients, and the development of 'expert' systems for the process control. The facility also gives researchers the ability to perform hands-on research in membrane and electrode fabrication, electrochemical testing, materials analyses and cell and device operation.

An analysis of site requirements at FSEC was conducted and an appropriate area to be refurbished into the IFCT was selected. State Fire Marshal regulations required that all laboratories must have an air handler system that uses 100% outside, non-recirculated air. As a result, it was necessary to install new air handlers for the IFCT. This was the single most challenging task, with many set backs before it was finally accomplished. Two labs were required for space.

The first lab was outfitted with two fume hoods, a 6-ft and an 8-ft. Four U-shaped benches were installed and much of the lab is devoted to analytical instrumentation. This includes an Altimira Thermal Programed Desorption system, a PMI BET Surface Area Analyzer, a Perkin Elmer FT-IR Spectrophotometer, Perkin Elmer Differential Scanning Calorimeter, Dionex High Pressure Liquid Chromatograph, JEOL Gas Chromatograph/Mass Spectrometer/Mass Spectrometer, Shimadzu UV-Vis Spectrophotometer, a Perkin Elmer Thermal Gravimetric/Differential Thermal Analyzer with attached Mass Spectrometer, and a Hiden pct system for analysis of hydrogen storage materials. This 1800 ft² laboratory contains instrumentation for material science analysis of fuel cell components.

The second lab is a 1100 ft² fuel cell laboratory. This Class B lab has capabilities ranging from those required for membrane electrode assembly fabrication to complete in-situ electrochemical diagnostics. There are three Scribner 850C fuel cell test stands, one Teledyne Medusa unit coupled with a Scribner 890C, 2 potentiostats, a sonicator and homogenizer for catalyst ink preparation, a screen printer, an enclosure for catalyst spraying, a dry box for membrane fabrication, a hot press under a canopy hood, three extra deep fume hoods (4-ft, 6-ft and 8-ft), a vacuum oven, and a high temperature oven.

Liquid Hydrogen Storage at Kennedy Space Center

PIs: L. Gu, D. Block, G. Bokerman, A. T-Raissi, and M. Basarkar
(Florida Solar Energy Center)

Research Period: September 2003 to September 2006

Summary

The liquid hydrogen and oxygen storage tanks at NASA Kennedy Space Center's (KSC) Pad A and Pad B have served the space launch operations for more than 40 years. Although these tanks are identical, the hydrogen boiloff rate was 750 gal/day for the Pad B tank and 300 gal/day for the Pad A tank. The main cause for the Pad B tank boiloff has been determined to be a void inside the vacuum space between inner and outer shells near the top of the tank caused by missing perlite insulation. The void area was discovered by viewing IR images taken at night by a KSC engineer. It is estimated that KSC losses approximately \$1 million per year due to liquid hydrogen and oxygen boiloff.

KSC plans to renovate the Pad B tank in the near future. Although there are many possible tank renovation options, the objective of the present project was to find out which options would be more realistic and economical. For example, one of these options is to add external insulation over the void area. The questions raised are, how large should the coverage area be and what should be the level of the thermal resistance. A second issue had to do with the tank insulation. Hollow glass microspheres are the leading candidate for replacing the perlite insulation. The microspheres provide improved thermal performance. While perlite is known to compact with age, the microspheres are expected to remain as free flowing particles. However, their limited use in cryogenic applications and their crush strength in the large tank have raised questions about particle behaviors.

Thermal simulations provide the only cost effective method to answer these questions. Thus, the objective of this project was to develop a computer model to examine the thermal performance of the Pad B LH₂ tank and to measure the experimental parameters that are needed for modeling of the granular effects of using glass microspheres as tank insulation. A detailed 3-D model was developed to simulate thermal performance of the tank with a void, a vacuum space without perlite between inner and outer shells. The model was validated against measured data, including boiloff rates, IR images, point temperatures and heat flux measurements and then parametric studies were performed. Experimental data from 3M Corp were also sent to KSC to support KSC's model efforts.

Following the extensive modeling, twelve conclusions and recommendations were made to KSC based on the investigation. These conclusions showed simulation results using the 3-D mesh are comparable with measured data, the heat transfer coefficient at exterior surface plays an important role in determining surface temperature distribution, boiloff rate is proportional to effective void interior surface equivalent emissivity and ambient conditions, the most important impact on boiloff rate is void size and the external insulation coverage may not be an effective method to reduce boiloff rate. See report for other conclusions and details.

Local Hydrogen Production via Catalytic Reforming of Fossil and Renewable Feedstocks

PIs: N. Muradov, F. Smith (Florida Solar Energy Center)

Research Period: June 2002 to December 2007

Summary

Economical, safety and other factors will eventually necessitate on-site manufacturing of liquid hydrogen at the NASA-KSC site. The objective of this project was to develop an economically viable process for local production of hydrogen from renewable and fossil-based methane-containing feedstocks with minimal environmental impact. In this project, research and development was conducted on two novel hydrogen production technologies: (i) direct reforming of landfill gas (LFG) to syngas and its further processing to H₂, and (ii) catalytic pyrolysis of methane to hydrogen and carbon.

The advantages of direct reforming of LFG are that it does not require preliminary recovery of methane from LFG, which simplifies the process. The thermodynamic analysis of CO₂ reforming of methane using AspenPlus™ chemical process simulator was conducted. Efficient and stable catalysts for the direct reforming of LFG were developed and tested. The catalytic activity of a number of commercial and synthesized transition metal catalysts (Ni, Fe, Pt, Pd, Ir, Ru and Rh) was evaluated. Ni-based catalyst was down-selected for further evaluation and the operational conditions for its efficient and stable operation were determined. A pilot scale unit with the capacity of 1 SCFM of H₂ was designed, fabricated and successfully operated using CH₄:CO₂=1.3:1 mixture mimicking local (Cocoa) LFG composition. It was estimated that the local resources of LFG would be sufficient for production of 5 tons/day of hydrogen. A preliminary economic assessment indicates the cost range of liquid hydrogen product to be \$3.00-\$6.00 per kilogram depending upon the production capacity and whether or not carbon sequestration is added.

For the methane catalytic pyrolysis process, its advantage is that it allows production of hydrogen and clean carbon, with no or minimal CO₂ emissions. The thermodynamic analysis of methane pyrolysis in two different regimes (thermo-neutral and external heat input) using AspenPlus™ chemical process simulator was conducted. Experimental data showed fairly good agreement with the simulation results. Comprehensive catalyst and process development studies for the methane pyrolysis reaction were conducted. Characterization and structural studies of carbon products of the process were conducted and potential markets for carbon products were evaluated. The technical feasibility of converting citrus waste products (e.g., citrus pulp pellets, CPP) into high purity hydrogen with the yield of 0.55 L of H₂ per gram of CPP was also demonstrated.

The research output consisted of four patent applications, 27 publications, 17 presentations, and support for two graduate students.

Photoelectrochemical Water Splitting for Hydrogen Production Using Multiple Bandgap Combination of Thin-Film- Photovoltaic-Cells and Photocatalyst

PI: N. Dhere (Florida Solar Energy Center)

Research Period: July 2002 to September 2006

Summary

One of the NASA research activities was to identify, characterize, and simulate a series of technologies that could be used for hydrogen production at NASA Kennedy Space Center (NASA-KSC) using locally available sources. This project examined the production of hydrogen from solar energy. To produce hydrogen by water splitting, the operating voltage of conventional photovoltaic (PV) cells cannot supply the overvoltage required. Thus, the objective of this project was to research and develop photoelectrochemical (PEC) cells that can supply the required voltage for water splitting by constructing a multiple bandgap tandem PV cell and a photocatalyst that can be activated by infrared (IR) photons transmitted through the PV cell. The proposed concept is different from conventional PEC water splitting by using multiple band gap combinations. The advantages for this PEC cell concept is that the PV cells are not in contact with the electrolyte solution, thus reducing the problems of corrosion and the photocatalyst is not grown directly over the PV cell as is the case with solid-state tandem PV cells.

The research conducted in this project was based on development of CIGS2 polycrystalline-thin film solar cells for use in the PEC process. CIGS2 thin film solar cells have the advantages over other types of solar cells of lower cost potentials, achieving large area depositions and integral interconnects and they do not suffer from intrinsic degradation.

The research developed P-type transparent and conducting layers, CIGS2 and CdTe thin film cells with transparent and conducting back contacts, suitable electrolytes with high conductivity and ruthenium oxide, ruthenium sulfide and ruthenium-iron sulfide photoanodes. Over the course of the project, the results gave a photovoltaic efficiency of conventional CIGS2 cells of 11.99% at an open circuit voltage of 830 mV. The calculated PEC efficiency for this configuration was 8.78% (solar to hydrogen).

In another experiment, the PEC hydrogen generation efficiency using two CIGS2 thin-film solar cells on transparent and conducting back contacts, connected in series with a RuS₂ anode and a platinum cathode under AM1.5 illumination. The PEC efficiency was calculated as 2.99%. This efficiency is lower than the CIGS2 and CdTe cycle because of the lower operating voltage of the CIGS2 pair. This efficiency can be improved by optimization of the operating voltage and increasing the efficiency of the photoanode for oxygen evolution.

As a result of the research there were 9 technical papers, 4 graduate student theses and 14 presentations. The research supported 1 Ph.D and 3 M.S students.

System Analysis of Hydrogen Production and Utilization at KSC

PIs: A. T-Raissi, M. Elbaccouch, K. Ramasamy, J. Baik
(Florida Solar Energy Center)

Research Period: January 2003 to December 2007

Summary

The objectives of this project were to identify, characterize, and simulate a technology for hydrogen production for NASA-KSC from locally available sources. This activity will establish a baseline for the future procurement and use of hydrogen propellants at NASA-KSC. Chemical Process Simulators (CPS) were used to generate highly detailed and accurate process models for use in chemical plant designs. Aspen Technology's Aspen Plus is among the most widely used CPS platforms by leading companies in the process industries. The approach of the project is to generate gaseous and liquid hydrogen, under steady state conditions, sufficient for several NASA space shuttle mission. The project consisted of two tasks as follows.

Task 1 -- Chemical Process Simulation of Used Oil for the Liquid Hydrogen Production. The objective of this task was to simulate an economically viable process for the production of liquid hydrogen by steam reforming used automotive lubricating oil. The simulation was carried out using Aspen Plus™, Aspen Adsim™, and Aspen Icarus™ chemical process simulators. The reformer was simulated as a Gibbs reactor to reform the large oil molecules. A water-gas shift unit, simulated as an equilibrium reactor, was used to enhance the production of hydrogen and a flash separator was used to remove excess water from the product stream. The off-gas is burned with air in a combustor and the generated energy is used to heat the processing units. Aspen Adsim™ was used to simulate the adsorption process of the pressure swing adsorption (PSA). A hydrogen liquefaction unit, simulated as a Claude densifier cycle, was used to produce liquid hydrogen. Aspen-Icarus™ is utilized to develop a detailed capital costs breakdown for the plant.

Task 2 -- Aspen Plus Process Model for the Production of Gaseous Hydrogen via Steam Gasification of Bagasse. The objective of this task was to simulate a chemical plant for the production of hydrogen from bagasse using Aspen Plus Chemical Process Simulator with no heat generation. The goal of the simulation was to design and optimize the performance of a directly heated gasification system that converts bagasse into gaseous hydrogen. The Aspen model consists of four sections: 1) a dryer section to partially dry the bagasse, 2) a gasifier consists mainly of a bagasse combustion zone, and a gasification zone to volatilize the bagasse feedstock, 3) a gas clean up section to purify the hydrogen product, and 4) a pressure swing adsorption unit to recover the hydrogen at desired purity levels. A fraction of the bagasse was used as a fuel and directed into combustor reactors to fire up the plant. The temperatures of the combustor reactors in the gasifier section were set at 1550°C, and the generated heat was used to heat up the plant's reactors and flow streams. All other process units operate adiabatically. 900 kg.hr⁻¹ of bagasse was used as the feed stock of the plant to produce 17.4 kg.hr⁻¹ ultra pure hydrogen product.

The research results in 13 publications and 11 presentations.

Zero-Boil-Off Liquid Hydrogen Storage Tanks

PI: J. Baik (Florida Solar Energy Center)

Research Period: September 2003 to September 2006

Summary

The Florida Solar Energy Center and NASA KSC have conducted a collaborative research project with the objective of increasing the density of cryogenic propellants for launch vehicle applications. Technologies that provide for the densification, conditioning, transfer and storage of cryogenic propellants can reduce gross lift-off weight of a launch vehicle by up to 20% thereby increasing the vehicle's payload capacity. NASA KSC has years of experience handling cryogenic propellants, but all with saturated liquids. This work focuses on using existing cryogenic technology to densify hydrogen, and developing a test bed where densified propellant handling techniques can be researched.

FSEC and NASA KSC have designed a densified liquid hydrogen test bed that uses a Gifford-McMahon cryocooler to refrigerate hydrogen inside a 150L storage tank. The test bed is located at FSEC and has an integrated refrigeration and storage system with multiple capabilities. The volume of inner storage vessel was limited to 150 liter by the facility safety regulation code. The aspect ratio of the vessel was optimized by vessel material, operating temperature, thermal analysis of heat conduction and radiation heat transfer from ambient. Heat pipe technology was selected to extend the cold head of cryocooler down to the bottom of storage vessel. Operating temperature, pressure and thermodynamic properties of working fluid in the heat pipe can provide heat pipe design parameters such as material choices and dimensions. A pressure build-up unit was employed to control internal vessel pressure by evaporating stored liquid hydrogen without any vent loss. It also allows self-pressurization of the system in a short period of time to drain and/or transfer stored liquid hydrogen to other storage tanks and applications. The top plate of the vessel and its dewar necks were designed to maximize reconfiguration flexibility with flanged connections on the cryocooler interface and the outer vessel. This design allows full access to reveal components such as the cryocooler cold head, heat pipe, and copper braids structures out of the vessel when repairs and future modifications are needed.

As a preliminary densification test, a nitrogen liquefaction and densification tests were performed to exercise subatmospheric operating condition for subcooled cryogen. Then, the test bed successfully demonstrated hydrogen liquefaction and densification processes at 16.5K followed by long term ZBO liquid hydrogen storage. The test bed successfully performed 7.2~25 L/day of 16.5K densified liquid hydrogen demonstration from ambient gaseous hydrogen using a G-M cryocooler. A series of ZBO storage tests proved that the system can store densified liquid hydrogen without any boil-off loss by ~ 1 hr/day of the cryocooler operation.

The research resulted in eight publications and nine presentations.

A Reliable, Efficient and Compact Reverse Turbo Brayton Cycle (RTBC) Cryocooler for Storage and Transport of Hydrogen in Spaceport and Space Vehicle Applications

PIs: L. Chow, J. Kapat, Q. Chen, L. An, T. Wu, K. Sundaram
(University of Central Florida); C. Him (FSI); N. Dhere (Florida Solar Energy Center)

Research Period: July 2002 to September 2007

Summary

The objective of this five year project was to design a reliable, compact, lightweight, and highly efficient cryocooler for distributed cooling of liquid hydrogen systems for spaceport applications and to develop an appropriate integrated compressor/motor system for the said cryocooler. For many NASA space missions, cooling capacities much higher than 2 watts are estimated to be required. This effort in developing a light weight, compact and higher cooling capacity cryocooler will be highly beneficial for these applications. To accomplish the objective project, a reverse turbo Brayton cycle cryocooler was researched and developed. A key component was on the development of an integrated motor/compressor designed for use in the cryocooler. This cryocooler will be capable of extracting a few tens of watts (20-30 watts) of heat at liquid hydrogen temperature (~18 K).

All the previous attempts of cryocoolers by NASA for zero boil off of cryogenic propellants in space have cooling powers of less than 2 watts at liquid hydrogen temperature. These versions of flight-like cryocoolers would be more appropriate for cooling of sensors and super conducting materials in a spacecraft. The cryocooler designed under this project with a few tens of watts of cooling power at liquid hydrogen temperature will be ideal for ZBO of cryogenic propellants in NASA's future robotic missions to Mars and for other human space missions. The R&D activities under this program cover the design and thermodynamics of a high efficient cryocooler and development of a highly efficient, compact, reliable, high-speed and light-weight integrated compressor/motor setup for the cryocooler. Suggestions for improvement in the integrated compressor/motor setup were provided in addition to heat exchanger (HEX) design and friction and wear reduction techniques that help in the betterment of the system performance. Applications of the designed cryocooler for future NASA needs were also addressed.

- 1) It is possible to support high speed machinery (integrated compressor/motor system) on off-the-shelf bearings with proper balancing, alignment and aerodynamic optimization.
- 2) It is not advisable to use a mechanical coupler for high-speed rotating machinery.
- 3) Less the number of rotating parts in conjunction, better is the design for high rigidity and rotordynamic stability.
- 4) Tip gap plays a very important role in deciding the performance of a mesoscale centrifugal compressor.
- 5) A proper diffuser design (without flow separation) is a must for realizing high compressor efficiency.
- 6) A high effectiveness HEX design is a key enabling technology for a high system COP.

The research resulted in one patent, 24 publications, 18 presentations, and support of ten graduate students.

Development of Cryogenic Shape Memory Actuator Materials for Switches, Seals and Valves

PI: R. Vaidyanathan (University of Central Florida)

Research Period: July 2002 to October 2007

Summary

Shape memory alloy actuators are widely recognized as having the following advantages for space-related applications: (i) high power/weight and stroke length/weight ratios (ii) integration of sensor and actuator in a single element (iii) clean, debris-less, spark-free operation and (iv) ability to function in zero-gravity environments with small, controlled accelerations. Shape memory alloys (SMAs) when deformed can produce strains as high as 8%. Heating results in a phase transformation and associated recovery of all the accumulated strain, a phenomenon known as shape memory. This strain recovery can occur against large forces, resulting in their use as actuators.

The goal of this project was to lower the operating temperature range of shape memory alloys in order for them to be used in hydrogen related technologies. The immediate benefit to NASA is the development of a shape memory thermal conduction switch for application in cryogenic liquefaction, densification and zero boil-off systems. Even though a wide range of alloys are found to exhibit the shape memory effect, NiTi alloys are of particular interest owing to the best combination of material properties coupled with substantial strain recovery associated with the phase transformation. In NiTi, the phase transformation usually occurs in a single step from the high temperature austenite (B2, cubic) phase to the low temperature martensite (B19', monoclinic) phase or vice versa. Addition of Fe, introduces an intermediate trigonal R-phase. The emphasis of this project was on the R-phase transformation in NiTiFe alloys.

The project results made theoretical as well as applied contributions to understanding and using R-phase transformations in the ternary NiTiFe shape memory alloy system. Applied aspects include alloy development by recourse to arc melting followed by thermomechanical processing and a range of characterization techniques that include SEM, TEM, DSC, dilatometry, DMA, and indentation. The alloys were also used in prototype thermal conduction switches. Theoretical aspects include in situ neutron diffraction measurements during loading and cooling at Los Alamos National Laboratory. Thus, valuable information on deformation mechanisms was obtained.

From this funded work two patent applications have been filed and two patents have been disclosed. In addition, 12 publications and 21 presentations have resulted, and seven graduate students have been trained. Two of the students were awarded best theses awards in the UCF College of Engineering and Computer Science. Also various aspects of this project benefited from concurrent synergistic funded efforts from the National Science Foundation (a CAREER award), UCF-UF's Space Research Initiative (SRI), NASA KSC and Arctic Slope Regional Corporation (ASRC). A new project funded by NASA has just been initiated at UCF that leverages the knowledge and experience gained from this project for application to NiTiPt and NiTiPd alloys. Another separate project from ASRC is also expected to use NiTiFe springs in a convection-based heat-pipe type thermal switch.

Genetic Engineering to Enhance Biological Hydrogen Production

PI: W. Self, D. Ganyc, L. Halvorsen (University of Central Florida)

Research Period: June 2005 to September 2007

Summary

Conversion of lignocellulosic biomass to hydrogen, and potentially other fuels, can be a vital part of NASA's goal of deep space exploration. Recent NASA directives include missions to the Moon as well as Mars. One of the limitations to these missions is long-term fuel supplies. The ability to recharge fuel cells will require novel technologies to supply renewable sources of hydrogen. These renewable sources can be achieved using biological sources. The development of biological catalysts that can convert any form of biomass to hydrogen (and other potential fuels such as ethanol) thus has great significance for long term exploration of space.

The goal of this project was to genetically engineer metabolic pathways in bacteria to enhance the hydrogen yield generated from oxidation of the polymers (sugars) by catalyzing the reduction of protons with electrons using enzymes termed hydrogenases. Using engineered bacteria, the fermentation of sugars derived from biomass can be coupled with hydrogen production. The project first demonstrated that genetic engineering of metabolic pathways can enhance hydrogen production in the model system of *Escherichia coli*. From this result, a similar strategy was implemented to develop a hydrogen producing microbe that can efficiently degrade plant biomass, *Erwinia chrysanthemi*. Next, optimization of the formate hydrogenlyase (FHL) complex was accomplished in order to determine whether the approach was feasible for long term hydrogen production from plant biomass and to ensure that the engineered system is applicable for *near term* hydrogen production from plant biomass

Results on the regulatory systems of the FHL complex have revealed a link between selenoprotein synthesis and the regulation of the FhlA transcriptional activator. This result implies that *E. coli* has some type of sensory mechanism that monitors the intracellular levels of available selenocysteine. This mechanism is in turn able to modulate the amount of selenocysteine requiring enzymes being transcribed by directly affecting the expression of the *fhlA* protein. Based on past research, the expected result was that the highest amount of FHL complex activity would result with the combined expression of *fhlA165* along with a *hycA* mutant background, however, our result showed the opposite. The combination of these two mutations results in a phenotype having no detectable FHL complex activity. However, the fact that increasing the capacity for selenoenzyme synthesis, by transforming into these same cells the pSUABC plasmid, fully recovers this phenotype and provides strong evidence that selenoprotein synthesis is involved.

The research has resulted in one publication, three presentations and work for two graduate students.

Highly Selective Nano-Mems Low Temperature Hydrogen Sensor

PIs: S. Seal, H. Cho
(University of Central Florida)

Research Period: September 2002 to September 2007

Summary

Hydrogen safety and handling remain as top priorities to NASA operations and these concerns have been the prime motivation for this proposed research. Thus, the objective of this research was to develop nanotechnology based room temperature and low energy hydrogen (H₂) sensors with high sensitivity, selectivity, repeatability and rapid response times.

Currently available sensors are a variety of experimental (metal-oxide-semiconductor (MOS)-based, catalytic resistor, acoustic wave and pyroelectric) and commercial (catalytic combustion, electrochemical, semiconductor, and thermal conductivity) based technologies. They are based on different principles, but each as major drawbacks. Normally these sensors work at high temperatures (>80C – 400C). The very low sensitivity of these sensors at room temperature and low concentrations of H₂ has resulted in poor responses and recovery times. In addition, there are only few manufacturers, which guarantee the cross sensitivity to other poisonous gases and no claims are made regarding the suitability of these sensor-devices for sensing H₂ on other planetary conditions, which is an essential requirement for NASA. Thus, the commercial sensors currently available in the market are designed only to meet the atmospheric conditions on the earth's surface and modifying the sensor material properties to meet the NASA's over all requirements is imperative.

In the recent years, nanotechnology has emerged as an attractive field for the development of novel materials having unusual properties. To solve the hydrogen sensing problem, we have developed sol-gel-nanocrystalline indium oxide (In₂O₃) doped tin oxide (SnO₂) sensors, in the form of thin film/nanowires/nanofibers, for room temperature hydrogen sensing. The nanocrystalline thin film sensor is incorporated into the microelectromechanical system (MEMS) device to achieve high hydrogen sensitivity and selectivity with fast detection and recovery at room temperature.

The effects of various parameters such as the air pressure, H₂ concentration as well as the MEMS design parameters such as the finger spacing and the number of fingers on the sensing characteristics have been evaluated. The present nano-micro integrated sensor shows large room temperature H₂ sensitivity (10³-10⁵, orders of magnitude) with high selectivity over carbon monoxide (CO) was able to detect H in He environment. The current H₂ detection and recovery time at room temperature lie within the range of 4-200 sec, depending on various parameters. New technological solutions for further reducing the response and the recovery time of the present nano-micro integrated sensor have been proposed. Nano-micro integrated sensor prototype has been successfully developed.

The research resulted in one patent, 23 publications, 25 presentations, and work for seven graduate students.

Metal Hydrides for Hydrogen Separation, Recovery and Purification

PI: M. Hampton (University of Central Florida)
D. Slattery (Florida Solar Energy Center)

Research Period: June 2002 to September 2006

Summary

At NASA's Kennedy Space Center (KSC) hydrogen is used for the space shuttle and other launch vehicles. As a result, huge quantities of liquid hydrogen are transported, transferred and stored at KSC. During the transfer of the hydrogen from the trucks to the storage dewars, significant quantities of hydrogen are lost during the cool down of the transfer lines and from flash evaporation as the high pressure cryogenic liquid enters the low pressure dewars. Additionally, during storage, hydrogen is constantly lost because of boil off.

In addition to the hydrogen that is lost due to transfer operations and boil off, NASA also loses hydrogen during purge operations. Prior to filling lines with liquid hydrogen, they must be precooled with liquid helium. After an operation, the residual hydrogen is purged, again with helium, in order to safe the systems. Both the hydrogen and helium in these operations is currently not recovered, leading to additional losses. Recovery of this lost hydrogen and helium could lead to substantial savings.

It was the loss of KSC's hydrogen and helium that led to this project. The project objective was to research and develop a hydrogen storage system that can recover both hydrogen and helium. Hydriding alloys of the AB₅ type are suitable materials for hydrogen storage applications because of their large hydrogen capacity, easy activation and rapid hydriding/dehydriding rates. One of these representative compounds that has been extensively studied is LaNi₅ a compound that absorbs hydrogen rapidly, reversibly and selectively. As a result, it is capable of not only absorbing hydrogen as it vaporizes during transfer operations, but also is potentially useful for separating hydrogen from the helium purge gas. Selective removal of the hydrogen would allow recovery of helium, in high purity, for future use.

The results showed that the alloy, LaNi₅, had the kinetics and capacity needed to remove hydrogen from a flowing stream of hydrogen and helium, thus allowing purification of both gases. Other results showed that the addition of aluminum to the alloy up to a level of 47 mole% provided improvement in the kinetics of hydrogen absorption without significantly reducing capacity. This incorporation of aluminum into the lanthanum nickel alloy will enormously reduce the weight and cost of the alloy required to purify hydrogen and helium.

In addition to being used to purify helium and hydrogen, LaNi₅ could also be used to capture the hydrogen currently lost to boil-off. While the hydrogen recovered could not be used for shuttle functions because of the requirement for liquid hydrogen, it could be used for other functions at the space center, such as fueling automobiles or buses. The project recommended that a system based on lanthanum, nickel, aluminum alloy be implemented at KSC for the purification of hydrogen and helium and the recovery of boil-off hydrogen.

Wireless Passive Sensors and Systems for Physical Sensors and Hydrogen Sensing Applications

PI: D. Malocha, (University of Central Florida)

Research Period: July 2005 to September 2007

Summary

The objective of this project was to develop passive, wireless and multi-sensor surface acoustic wave (SAW) sensors based piezoelectric materials. The NASA application's for these sensors cover a wide range of NASA needs that include temperature sensing in harsh environments of space or ground-based operations, liquid level sensing for hydrogen, oxygen, nitrogen or other cryogenic liquids, and hydrogen gas sensing.

The developed SAW sensors are passive, wireless, small and lightweight. SAW devices have no fundamental limitation in material or physical principles for wide temperature operation; from cryogenic temperatures to 1000 °C, with appropriate substrate material. In addition, the SAW sensors can be encoded to provide security and close proximity multi-sensor operation. Finally, the proposed SAW sensor is totally passive, which means there are no batteries or other source for a spark or ignition; critical for use in the hydrogen environment and the SAW device can be accessed remotely without external connections, removing cabling and interconnects to a sensor array.

The objectives of the research project were to build new and novel SAW wireless-passive sensors, to research the SAW components operation at cryogenic temperatures, to build new devices and test fixtures for hydrogen gas sensing, and to develop measurement and test procedures. The developed SAW devices use orthogonal frequency coded (OFC) SAW reflective structures to encode the signal and to send back the sensor information. The encoding technique is similar to multi-tone CDMA in terms of its implementation, where a transducer or reflector is built with the desired code A RF 250 MHz transceiver system has been built for sensor interrogation. This process shows the feasibility of a software-radio approach for data acquisition, post processing and sensor data extraction.

The use of OFC SAW sensor technology has been shown to be a viable platform for passive, wireless sensor systems. Initial work is very promising for the use of nano Pd thin films as a possible reversible room temperature sensor. New methods of the coding devices have been studied which will lead to lower collision effects in a multi-sensor system environment. Higher frequency devices have been demonstrated which will reduce the required antenna size and should increase range. Although great progress was made, more research is needed to make the SAW devices a commercial product.

Because of this effort, a number of NASA STTR proposals and contracts have been submitted and won. Nine students have been funded from this program, 11 publications and five presentations were done. In addition, collaborations are now established between the UCF group and NASA KSC, JSC, Langley, and Glenn. It is certainly our judgment that this has been an extremely fruitful program.

Densified LH₂ and LO₂: Transport Properties and Density

PI: S. Van Sciver (Florida State University)

Research Period: June 2002 to September 2007

Summary

The overall objective of this experimental program was to produce precision measured values for the thermal conductivity, viscosity and density of subcooled LO₂ and LH₂. The region of primary interest was subcooled liquid below the normal boiling point (56 K to 93 K for LO₂ and 14 K to 20 K for LH₂) and for pressures up to 0.7 MPa. The measurement precision was to be better than +/- 1%. The second objective was to establish facilities that can be used to investigate transport values in other cryogenic fluids of interest. No other similar facilities are currently in operation in the US. The project had three tasks as follows.

Task 1 --Determine the thermal conductivity of subcooled O₂ and H₂. The thermal conductivity of liquid oxygen and hydrogen have been studied extensively, however, available data do not extend below about 77 K in the case of oxygen and there are very few points below 20 K for hydrogen. These measured thermal conductivity values were obtained and were compared with the available experimental data in the literature and from Refprop, a NIST standard reference database code.

Task 2 -- Determine the dielectric coefficient and density measurement of subcooled O₂ and H₂. From the best knowledge, dielectric coefficients of liquid oxygen have only been measured either along the liquid-vapor saturation curve or above 100 K for compressed fluid. In addition for the case of subcooled liquid equilibrium hydrogen, the dielectric coefficient of has not been measured to very high accuracy and precision. These results give the dielectric coefficients measured for liquid oxygen below 95 K and for liquid hydrogen below 23 K both at pressures up to 1 MPa. The results are combined with the previously published data for liquid along the liquid-vapor saturation line to express the fluid density in terms of the dielectric coefficient embedded in the Clausius-Mossotti relation. This expression covers both the liquid and the gaseous state.

Task 3 -- Measure the kinematic viscosity of subcooled O₂ and H₂. Successfully measurements of the absolute dynamic viscosity of subcooled liquid oxygen over the desired the pressure and temperature domains was completed, but the measurements for liquid hydrogen were inaccurate.

The experimental effort developed three new measuring instruments. The first instrument was for measurements of the thermal conductivity (k) and dielectric coefficient (κ) of subcooled liquids. The second instrument was the development of a capillary tube viscometer and the third instrument was a dedicated ortho-para converter used to supply equilibrium hydrogen to both experiments.

The research produced 9 publications and six presentations.

Experimental and Numerical Investigations of Cryogenic Multiphase Flow

PIs: S. Van Sciver, Y. Hussaini (Florida State University),
J. Justak (Advanced Technology Group)

Research Period: June 2002 to December 2005

Summary

The purposes of this project were to experimentally measure and model solid hydrogen particle mass flow in liquid helium and two phase liquid/vapor flow or solid/liquid hydrogen flow for fluid handling systems. The project was a joint effort between the Cryogenics group at Florida State University (FSU), members of the School of Computational Sciences (SCS) at FSU and the Advanced Technology Group (a small business in Stewart, FL). The work focused on three main subtasks.

The first subtask was the development of an experimental test facility to produce and measure cryogenic multiphase flows. This facility is a flow visualization facility which has an overall length of 5 m and includes two visualization ports. Flow channels within the facility are suspended in a vacuum environment and surrounded by thermal radiation shields cooled by LN₂ and LHe natural circulation loops. The end stacks contain metal bellows pumps, each with a volume displacement of one liter and controlled by linear stepper motors. These components can force the liquid cryogenics to flow in either direction at precisely controllable volume flow rates up to 0.3 liters/s. The two phase flow facility is also capable of studying flows consisting of a mixture of solid hydrogen particles (sH₂-p) and LHe. To support these measurements, researchers have developed the capability to inject sH₂ particles into liquid helium.

The second subtask was development of a numerical simulation program to provide a synergistic approach with the experiments to study the production of hydrogen particles of uniform size and shape, their storage in the LHe carrier, and the multi-phase flow characteristics of the slurry comprising sH₂ in LHe. The simulations are first validated by the experiments followed by a simulation-based parametric study to guide future experiments. Liquid hydrogen droplet formation has also been addressed within the context of the incompressible Navier-Stokes equations for multiphase flows with the surface-tension model properly incorporated.

The third subtask was the development of mass flow sensors for measurements in two phase cryogenic flows. As part of this program, Advanced Technologies Group (ATG) developed a Fluid Optical Quality Sensor (FOQS) for cryogenic fluids. The capability to measure cryogen depletion instantaneously is critical when operating cryogenic turbo-machinery. The Fluid Optical Quality Sensor (FOQS) provides a means of measuring fluid quality for a wide range of flow systems. In addition, a laminar two phase mass flow meter was developed at FSU. Both these mass flow sensors were tested in liquid nitrogen and liquid helium using the experimental multiphase flow facility at FSU.

This work produced six publications, five presentations, no patents and one MS thesis.

Improved Hydrogen Yield from Florida Specific Biomass Gasification Using a Pilot Scale Gasification Unit

PI: R. Srivastava (Florida International University)

Research Period: Julyd 2002 to September 2007

Summary

Local production of hydrogen is of interest to NASA KSC because of economic, transportation safety, and energy security considerations. Thus, this project conducted R&D on hydrogen production from biomass through thermochemical processes. Gasification (thermochemical methodology) yields fuel gas that can be used in variety of power options. During the initial phase, citrus peels and sugarcane bagasse were identified as promising local biomass resources in Florida due to their overabundance and favorable market value. The farmland acreage dedicated to citrus almost exceeds 800,000 acres and the citrus industry generates more than 1 million tons/year of citrus waste residue (dry basis). Biomass fuels consist of moisture ranging from 5 to 35%. At the temperature above 100°C, the water is removed and converted into steam. Biomass does not experience any kind of decomposition in the drying stage. A key element in planning a biomass to hydrogen facility is to locate a plant that will have ready access to adequate feedstock supplies.

The primary objectives of the project were to design, fabricate, and operate a pilot-scale biomass gasification unit, validate the unit's performance and identify economic and technical barriers. The research was focused on the biomass gasification testing in a pilot-scale gasifier of 10-100KW range. Effort was directed towards maximizing the hydrogen yield in the synthesis gas. Results assessed the technical and economic potential of producing hydrogen from citrus peels obtained from Citrus World Inc. in Lake Wales, FL. The citrus pellets had approximately 14% (wt.) moisture content.

Gasification is a two-step process in which a solid fuel (biomass) is thermochemically converted to a low- or medium-energy-content gas. A highly critical factor in the high-energy efficiency of the gasification process is that of the gasifier (primary reformer) which consists of four stages—drying, pyrolysis, oxidation and reduction. The gasifier used was procured from Community Power Corporation (CPC) of Littleton, CO. The gasifier is a downdraft unit, fully automated system that has the ability to convert a variety of woody biomass residues into syngas.

The report also includes results on the feedstock preparation, feedstock handling, feedstock performance, hydrogen yields and potential problems identified during the pilot scale experiments.

The results for biomass gasification of citrus pellets show that hydrogen can be produced economically at an average \$7.54/GJ for 10-100KW range pilot scale gasification unit. Previous literature studies have cited that hydrogen prices from \$6 – \$10 /GJ can be realized.

Numerical Simulation Model for Thermo-Fluid Analysis of Cryogenic Storage Systems with Zero Boiloff

PI: M. Rahman, S. Ho (University of South Florida)

Research Period: September 2002 to September 2007

Summary

Conventional methods of storing hydrogen are either as a compressed gas or as a cryogenic liquid. Liquid storage of hydrogen has a very significant advantage over gaseous storage because of its much lower storage volume and ease of regeneration of the fuel with demand. Conventional cryogenic storage tanks suffer loss of hydrogen due to boil-off of the cryogen induced by heat loss from the tank to the surrounding environment. In order to keep the inner pressure within the structural limits of the tank, the stored fluid needs to be periodically vented. The Zero Boil-Off (ZBO) concept has evolved as a means of storage tank pressure control by a synergistic application of passive insulation, active heat removal, and forced mixing within the tank. The goal is that the fuel can be stored for a very long time with almost no loss.

This report presents a numerical simulation study of steady state fluid flow and heat transfer in a cryogenic storage tank for liquid hydrogen using two and three-dimensional models. The tank model includes a tank with cylindrical wall and oblate spheroidal top and bottom, a heat pipe located along the axis of the tank, and one or more pump-nozzle unit(s) that collects fluid at the suction inlet and discharges at its nozzle face onto the cool tip (evaporator) of the heat pipe in order to prevent the fluid to boil off.

For a number of pump-nozzle units, the numerical simulations were done using an axis-symmetric model because of the nearly axis-symmetric nature of the problem. For one pump-nozzle unit, a three-dimensional model was employed since the axis-symmetry was no longer the case. It was found that the normal speed at the nozzle and tank dimension parameters significantly affect the mixing, cooling, and boiling of the fluid inside the tank. These parameters can be used to optimize the performance of the cryogenic system.

The results from the simulations for both models show that the increasing of the fluid speed discharged at the nozzle face improves both mixing effectiveness (increase average speed, decrease maximum-average temperature difference) and zero-boiling-off effectiveness (decrease maximum temperature). The numerical simulations give better understanding of the fluid flow and heat transfer phenomena needed for the design of a cryogenic storage tank for liquid hydrogen.

Prototype and Simulation Model for a Magneto-caloric Refrigerator

PIs: S. Bhansali, M. Rahman, S. Kim, S. Ghirlanda, C. Hernandez, C. Adams,
B. Bethala, L. Rosario, S. Sambandam
(University of South Florida)

Research Period: September 2002 to September 2007

Summary

Hydrogen liquefaction is necessary technology for satellite and space craft. The magnetocaloric refrigeration of this project is being explored as a highest efficient pathway for cooling hydrogen for storage and liquefaction. Realizing micro cryo-coolers that can operate at low temperature with high cooling capacity, and in a small size has been a challenge. This research makes a development of micro-cooling device which has compact size. This process required that magnetocaloric materials be exposed to an alternating magnetic field. Analysis and experimentation have positioned the investigators to both (a) demonstrate the feasibility of magnetocaloric refrigeration and (b) experimentally validate the critical parameters required for design of scalable cooling systems. Simulation of cooling hydrogen from 77K to 20K suggests a multi-stage GdSiGe based magnetocaloric refrigeration system.

Thermodynamic analysis was carried out for a magnetic refrigeration system for near room temperature application using Gd as the magnetic material. The conceptual design and analysis of a magnetic refrigeration system near hydrogen liquefaction temperature was established based on two prototypes with circular and trapezoidal microchannels. In aspect of fabrication, the microfabrication processes and fabrication of trapezoidal flow channels in silicon was developed and tested.

The stability of Si_3N_4 as a diffusion barrier in deposition of GdSiGe thin films on Si was studied. Thin films of GdSiGe were deposited on PECVD nitride coated Si substrate. The films were annealed in vacuum to crystallize the GdSiGe desired phase. SIMS analysis of the interface of GdSiGe/ Si_3N_4 /Si films indicates a breakdown of the SiN diffusion barrier with depletion of GdSiGe films into silicon nitride and Si upon annealing at 1150°C. It is hypothesized that the dangling hydrogen bonds in Si_3N_4 contribute to the breakdown. The AlN/ SiO_2 layer is also used as barrier layer for GdSiGe annealing. The result shows that the layer has good role and it prevent diffusion of GdSiGe into the Si wafer.

The trapezoidal microchannels were designed with circular and trapezoidal microchannels. The eight microchannels with 150um deep in 2inch wafer were fabricated using MEMS technology. The combined etching of 250 μm formed the inlet and outlet ports to flow refrigerant. The in-situ temperature sensors through deep impurity diffusion were installed into the wafer and tested by changing the temperature. GdSiGe block was assembled with the microchannel and its prototype of microcooler was shown in the presentation. The cooling test are carried out by applying electromagnetic field to the GdSiGe, and obtained temperature change. The constant temperature chamber was made by using insulating material and the lower temperature than room temperature was obtained by liquid nitrogen.

Smart Porous Metal-Organic Frameworks (MOFs) for Hydrogen Recovery and Storage

PIs: M. Eddaoudi, M. Zaworotko, B. Space (University of South Florida),
J. Eckert (Los Alamos National Laboratory) and
A. T-Raissi, N. Mohajeri (Florida Solar Energy Center)

Research Period: January 2005 to November 2007

Summary

Advances in the fast growing field of microporous metal-organic frameworks (MOFs) have led to numerous developments. Specifically, the chemistry of MOFs has provided a range of low-cost porous crystalline materials assembled from molecular building blocks (MBBs) that exhibit high stability, tunable properties, and porosity. Synthesis of metal-carboxylate polyhedral frameworks and molecules based upon metal-carboxylate building blocks has attracted interest for their properties such as porosity, H₂ storage and magnetism. Though a myriad of crystalline porous carboxylate based MOFs have been synthesized and structurally characterized, many remain unexplored for their potential as H₂ storage media. The nature of these structures is such that they are simple and inexpensive to prepare, they are modular and can be designed to contain accessible windows and nanoscale cavities (often decorated with adjustable open metal sites) suitable for H₂ sorption.

Better hydrogen storage materials will have a far-reaching impact on future aerospace technology. Recently, applications of rigid MBBs have led to the development of a wide range of MOFs, from fused metal-organic polyhedra to zeolite-like MOFs (ZMOFs), with large accessible 3-D pores decorated with adjustable periodic organic and inorganic moieties suitable for hydrogen uptake. Most recently, systematic studies of MOFs have indicated that increasing the number of benzene rings in the scaffold of a MOF greatly improves the amount of hydrogen uptake. Furthermore, Inelastic Neutron Scattering (INS) studies suggest that MOFs can contain several types of hydrogen binding sites ranging from organic components to the metal constituents of the framework, including results that indicate open metal sites may increase H₂-framework interactions. Preliminary studies have demonstrated that MOFs have the ability to store larger amounts of non-cryogenic hydrogen than amorphous porous carbon and inorganic zeolites. Further, the facile tunability of the MOF constituents and pore size has reinforced the belief that materials with superior H₂ storage capacity are achievable.

Thus, the specific objectives of this project were to synthesize and characterize viable porous MOFs for H₂ storage, to develop a better understanding of the interactions between sorbed hydrogen with the organic and inorganic constituents of the sorbent MOF by means of INS and computational studies and to construct made-to-order cost-effective MOFs that exhibit superior hydrogen storage capacity. The results of this project provide a basis for developing selected metal-organic frameworks as high-capacity hydrogen storage materials for onsite H₂ recovery, purification and storage.

The project's research output has included the award of a similar project by the U.S. Department of Energy (Project # DE0FG02-07ER4670) and two publications and three presentations.

Surface Acoustic Wave (SAW) Sensors for Hydrogen and other Gas Detection

PI: V. Bhethanabotla (University of South Florida)

Research Period: September 2002 to September 2007

Summary

Design, construction and testing of inexpensive, solid state sensors that respond sensitively, selectively and rapidly to hydrogen and other gases are a NASA need. Acoustic wave devices have been known for their use in sensor applications and are capable of meeting the above requirements, as well as providing passive and wireless operation. To achieve the objectives for hydrogen sensors, the research approach was one that combined surface acoustic wave (SAW) transducer technology with nanomaterial sensing layers. For these SAW devices to be practical, advances in device fabrication, wireless communication, device packaging and sensing materials were necessary. Solid-state SAW devices are mass produced in current cell phone, TV and other radio frequency uses, thus, a suitably designed hydrogen sensor can be similarly produced inexpensively.

The research approach was to leverage the mass, electroacoustic and elastic response mechanisms of SAW devices, with the advantages afforded by the nanomaterials of Pd-alloys as the sensing layers. The research constructed field devices using suitably designed high frequency SAW devices. Results of the research is summarized as (1) the setting up of an acoustic wave sensors laboratory with full sensor testing capabilities, (2) the development of several candidate prototypes for hydrogen sensors, (3) the development and evaluation of various nanomaterial sensing layers for hydrogen detection and sensing at room temperature in a surface acoustic wave sensor configuration, (4) the development of a high frequency (100 MHz) thickness shear mode organic vapor sensor demonstrating superior sensitivity, (5) multiple-scale modeling to understand sensor mechanisms and (6) the development of a novel hexagonal multi-frequency surface acoustic wave sensor, useful in chemical and biological sensor applications.

Specifically, Pd-coated single walled carbon nanotubes (Pd-SWNTs) have been developed and are emerging to be the best sensing materials tested so far in hydrogen sensor applications. Preliminary results indicate that these Pd-SWNTs are capable of several times more sensitivity compared to pure Pd nanomaterial layers, and possess excellent repeatability upon cycling with hydrogen exposures.

A hexagonal SAW device development is nearly complete, and is being tested in the detection of multiple biomarkers in specific applications to ovarian cancer detection, collaboration with the Moffitt Cancer Research Center at USF. Future sensor research is expected to yield commercially viable results.

Thermo Catalytic Hydrogen Production Via Oxygen-Free Methane Aromatization

PI: J. Wolan, E. Stefanakos, A. Kababji (University of South Florida)

Research Period: April 2004 to September 2007

Summary

One of the NASA research activities were to identify, characterize, and simulate a series of technologies that could be used for hydrogen production at NASA Kennedy Space Center. This work investigates the production of hydrogen from a biomass by a process that is a direct gas to liquid. The most important benefit of this process is that it is highly selective to pure hydrogen production with no green-house gas by-products. The bimetallic catalyst developed is molybdenum promoted H-ZSM-5 zeolite modified with various transition metal ions (TMI). These catalysts are prepared by the incipient wetness co-impregnation of the ammonium form of the zeolite, calcined in air at 500°C, and then reduced and activated following an in-house developed procedure.

For this project, bimetallic catalysts were prepared by incipient wetness co-impregnation of a ZSM-5 and H-ZSM-5 zeolite support. The supports were formulated and tested for use in methane non-oxidative aromatization to hydrogen and aromatic species. A novel 100% hydrogen-selective custom designed catalytic membrane reactor was utilized. In this design, no separation of products is required as hydrogen is selectively permeated through an internal membrane. This catalytic system has been designed to be selective for hydrogen production over benzene and thus is considered a novel technology as researched catalytic systems of this type are designed to be selective toward production of benzene.

In this study, the focus is on the production of hydrogen rather than the aromatic products which include ethylene, ethane, toluene and unreacted methane. The overall chemical reaction is considered highly endothermic, operating in the temperature range between 600-850°C. The large activation energy and high temperature reactions has been shown to affect the catalyst performance adversely through sintering and/or coking of the catalyst bed. Therefore, catalyst design, fabrication and pretreatment are critical.

The results for the rate of hydrogen production are:

- At 500°C up to 550°C and after 1 hour on stream, H₂ production rate was 36 sccm (based on 100sccm methane flow rate).
- At 600°C up to 650°C and after 1 hour 40 min total time on stream, H₂ production rate was about 10 sccm (based on 100sccm methane flow rate).
- Membrane selectivity to H₂ is approximately 100%; the calculated selectivity data for different catalyst systems is shown below.
- Aromatic compounds including benzene, toluene, ethane, ethylene and cyclohexane rates of production have not been determined, but conversion results are presented. CO and CO₂ conversion vs. temperature curves are also presented for different catalyst systems prepared.

Modeling and Optimization of Fuel Cell Systems for Aircraft Applications

PI: J. Ordonez, C. Luongo
(Florida Agricultural and Mechanical University-Florida State University)

Research Period: March 2005 to September 2007

Summary

The use of fuel cells for aircraft is an ever-growing concept in today's environmentally conscious world. NASA studies have indicated that fuel cells are becoming reasonably practical for propulsion in small aircraft and could be promising in future large-scale commercial aircraft. For these applications, it is important to understand the fuel cell-based power system from a system integration and power management perspective. Optimizing the integration of each component into the system and understanding the overall power system compatibility is essential for a successful design. Thus, the main objective of this project was to research and develop design concepts for implementation of fuel-cells on aircraft by modeling and optimization of the fuel cell systems.

The project results gave four major outcomes: 1. A library of fuel cells and fuel cell power network components were developed to facilitate a simulated test bed for fuel cell-based power systems. All of the models were developed in an electric network simulator (EMTDC) and include a solid oxide fuel cell (SOFC) stack, a proton exchange membrane (PEM) fuel cell stack, electrical converters (time-averaged models and switching models), and forms of energy storage. As a test case scenario, a fuel cell-based powertrain system was modeled and simulated for Cessna-like power range specifications.

2. Guidelines for the optimization PEM and SOFC internal structures were developed. Numerical results showed that the optimized single cells internal structure and stack external shape are "robust" with respect to changes in stoichiometric ratios, membrane water content, and total stack volume. The optimized internal structure and single cells thickness, and the stack external shape are results of an optimal balance between electrical power output and pumping power required to supply fuel and oxidant to the fuel cell through the stack headers and single-cell gas channels.

3. Models were developed and implemented in the Matlab-Simulink environment to guide the selection of hybrid fuel cell /gas turbine system configuration. A comparative study based upon performance parameters, such as SOFC power, turbine inlet temperature, and exhaust temperature was used to select a configuration among few candidates.

4. The modeling of renewable fuel cell (RFC) subsystems has been addressed. The models presented focus on the application of RFC subsystems to high altitude aircraft operations. Solid oxide cells were found to have performance disadvantages that prohibit dedicated galvanic and electrolytic cell configurations, specifically with respect to thermal management.

The full report (100+ pages) is available upon request. The research resulted in ten publications, seven presentations and the training of nine graduate students and 13 undergraduate students.