FINAL TECHNICAL REPORT

Executive Summary

Hawaii Energy and Environmental Technologies Initiative

Office of Naval Research

Grant Award Number N00014-09-1-0709

For the period April 1, 2009 to September 30, 2011

HNEI
Hawai'i Natural Energy Institute
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Final Technical Report for the
Hawaii Energy and Environmental Technologies (HEET) Initiative
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A. Executive Summary

This report summarizes work conducted under Grant Award Number N00014-09-1-0709, the Hawaii Energy and Environmental Technologies (HEET) Initiative, funded by the Office of Naval Research (ONR) to the Hawaii Natural Energy Institute (HNEI) of the University of Hawaii. The effort under this award continued a focus on critical technology needs associated with the development and testing of advanced fuel cells and fuel cell systems, an expanded effort on fuel processing and purification, and the exploration and utilization of seabed methane hydrates. This award also began new efforts relating to the interest of ONR in the use of Hawai‘i as a Model for Distributed Energy Systems for the Pacific Region. These efforts include new tasks addressing testing and evaluation of alternative energy systems, with initial activities in testing of heat exchangers for Ocean Thermal Energy Conversion (OTEC), grid storage, and photovoltaic systems. This represents the sixth award of the initiative.

Major accomplishments under the first grant award, Number N00014-01-1-0928, included the planning, design and construction of the Hawaii Fuel Cell Test Facility (HFCTF), which opened in May 2003. In partnership with industry, HNEI established test protocols and initiated a variety of long-term durability studies. The methane hydrates activities under the first agreement initiated studies to characterize hydrate thermochemistry and kinetics, hydrate microbiology and development of international collaborations.

Under the second award (N00014-04-1-0682), HNEI expanded its test capabilities with the addition of three fuel cell test stands at the HFCTF, including two for fuels purity studies. Tests to characterize the effects of contaminants in the hydrogen fuel were initiated. The third stand was designed for high speed dynamic testing for use in Hardware-in-Loop (HiL) work. Modeling and simulation of a fuel cell energy/power system for use in an unmanned underwater vehicle (UUV) was also completed and reported. Novel fuel cell component research was conducted to explore the use of biocarbons in fuel cell bipolar plates and development of enzymatic bio-fuel cells. A small effort in alternative fuel research focused on fuel processing and gas conditioning for hydrogen production. HNEI's activities in the area of methane hydrates included studies of hydrate destabilization phenomena, with shakedown testing of HNEI's destabilization facility and design and fabrication of a novel fiberoptic probe to identify sample aspects within the calorimeter sample cell using Raman spectroscopy. HNEI sponsored and manned the organizing committee of the 4th International Workshop on Methane Hydrates that took place in Victoria, British Columbia, Canada on 9-11 May 2005.

Under the third award (N00014-06-1-0086), the capacity of the HFCTF was again expanded, by increasing the number of test stands and modifying the existing test stands for increased performance. The dynamic HiL test stand was modified to enhance response and to improve operating flexibility, safety, and test stand reliability. Simulation tools for evaluation and screening of fuel cell systems for UUV propulsion systems were developed. HNEI continued research on fuel processing and gas conditioning for hydrogen production, focused on sulfur

removal from fuel gas using activated-carbon-based sorbents, and reformation of seafloor methane for use in underwater fuel cells. Work continued in the development of novel fuel cells, specifically in the areas of biocarbons for fuel cell use and development of enzymatic bio-fuel cells. HNEI's activities in the area of methane hydrates included an expanded effort in hydrate destabilization with development of a novel instrument that combined spectroscopy and calorimetry to study reagent-induced decomposition of the hydrates. As part of our goal to promote international collaboration, HNEI personnel participated in a multi-national research cruise off New Zealand in June and July 2006.

In the course of the fourth award (N00014-06-1-1055), more test stands were added to the HFCTF and several existing stands were modified to allow testing of small stacks. Several test stands were used to support Ion Tiger, an ONR-funded unmanned aerial vehicle (UAV) project. Research focused primarily on understanding the performance impact of contaminants present in the anode and cathode feed streams. The HiL test stand was also upgraded, allowing testing of fuel cell stacks up to 1 kW. Simulation tools were modified for evaluation of fuel cell systems for propulsion of a UAV. A plasma reforming effort was initiated with the design, construction, and testing of two different plasma arc reactor designs. The reverse-vortex reactor performed better than the planar plasma, gliding arc design. In support of the DARPA-sponsored Direct Carbon Fuel Cell research project at SRI International (SRI), HNEI prepared biocarbons from various biomass feedstocks to aid in optimizing performance of SRI's carbon fuel cells. Development of enzymatic bio-fuel cells continued, focused on enzyme immobilization utilizing macroporous chitosan polymer composites. The methane hydrates activities included significant progress in understanding hydrate destabilization using thermodynamic inhibitors. The impact of seafloor methane from hydrates on the marine environment was explored via both experiments and modeling. HNEI again supported and helped organize the 6th International Workshop on Methane Hydrate R&D that was held in Bergen, Norway in May 2008. The workshop was attended by scientists, engineers, and other stakeholders from 12 countries and a meeting report is available from the Naval Research Laboratory (NRL).

Under the fifth award (N00014-07-1-1094), several upgrades to test stands and infrastructure were implemented. Research included work on SO_2 contamination mechanisms and recovery, testing of Protonex hydrogen/air stacks under pure oxygen in support of the Naval Undersea Warfare Center (NUWC) at Newport, RI, development of a new segmented-cell flow-field design, and continued testing and analysis in support of Ion Tiger. Efforts to characterize a non-thermal plasma reactor for methane reforming were continued. Parametric tests were conducted and system performance was characterized using various metric features. HNEI continued providing biocarbons to SRI in support of its DARPA-sponsored work with direct carbon fuel cells. HNEI also completed a study of carbonization of sewage sludge from a treatment plant on O'ahu. Cost estimations of HNEI's commercial-scale Flash Carbonization™ reactor were completed, revealing the high cost of providing compressed air for operation of a pressurized catalytic afterburner (CAB) needed to meet emissions regulations. The focus of the enzymatic bio-fuel work continued to be enzyme immobilization utilizing macroporous chitosan polymer composites that support both mediator-based and direct-electron-transfer mechanisms. The methane hydrates activities included laboratory and analytical investigations of hydrate destabilization by chemical reagents, comparison of obtained data with models developed to predict the fate of methane released from the seafloor into the water column, experimental and modeling efforts examining the impact of methane from hydrates on the marine environment,

exploratory laboratory studies of H_2 storage, and the promotion of international R&D partnerships via support and help in organizing the 6th International Workshop on Methane Hydrate R&D held in Bergen, Norway in May 2008 and the 7th workshop held in Wellington, New Zealand in May 2010.

In the course of this award (N00014-09-1-0709), work was continued under the Fuel Cell Testing and Evaluation tasks. Test stand and infrastructure upgrades focused on increasing the maximum station power test capability to 5 kW to support Navy UUV interests.

Component and stack testing encompassed air contamination studies and investigations concerning the impact of manufacturing defects on fuel cell performance. The air contamination work covered component degradation during SO_2 contamination and performance recovery, and mechanistic modeling of SO_2 adsorption on catalysts consisting of carbon-supported platinum nanoparticles. HNEI's segmented cell system which includes cell hardware and a data acquisition system was used to characterize the impact of defects in the MEA. Defect location was found to be an important element, with defects located at an outlet resulting in more significant impact on performance.

Fuel cell Hardware-in-Loop (HiL) activities concentrated on Ion Tiger power pack characterization. Mission load profiles were used to evaluate the Protonex on-board fuel cell performance recovery method and to evaluate use of the 12-volt battery pack to provide power during fuel cell regeneration events. Performance comparisons were obtained for two types of lithium ion batteries. UAV system simulations were developed in a Matlab/Simulink environment for different system configurations (non-hybrid, traditional full hybrid, and novel partial hybrid) to study the impact of adding battery packs (weight) and controller hardware (weight and power losses) on the flight duration of the UAVs for a given propulsion and ancillary load profile.

HNEI produced and characterized biocarbons from corncob, oak wood and sweet gum wood in support of biocarbon fuel cells. The two woody materials were supplied by the Dow-Corning Corporation that employs charcoal as a reductant to manufacture silicon from quartz. The research resulted in two publications and a third that is in preparation. Development of enzymatic bio-fuel cells also continued, focused on enzyme immobilization utilizing macroporous chitosan polymer composites. In addition, development of unique *in situ* characterization techniques to investigate immobilization phenomena and processes was initiated. These activities have helped to secure additional funding from the Air Force Office of Scientific Research for a Multi-disciplinary University Research Initiative project and from the National Geospatial-Intelligence Agency for a postdoctoral fellow research project.

The work under the Technology for Synthetic Fuels Production task included a biofuel characterization planning. This subtask sought to identify biofuel components in support of Navy operations in tropical island settings. Pathways for bioenergy systems were explored, fit-for-purpose screening standards for F-76 and JP-5 fuels were summarized, and special equipment requirements for fuel quality research program needs were presented.

The second subtask involved plasma arc processing of fuels to produce hydrogen-rich fuels for fuel cell applications. Specific accomplishments were achieved in characterization of the performance of the reformer on methane over a range of conditions, additional design and

selection of fuel system components required for delivery of fuel to the reactor, and initial work on a numerical model of the plasma reactor system.

Thermocatalytic conversion of syngas into liquid fuels constituted the third subtask. A Fisher-Tropsch reactor system was designed for production of high-quality clean fuels from biomass-derived synthesis gas. The system consists of three major subsystems: a pre-reactor subsystem to meter reactants to the reactors, the reactor subsystem comprising the synthesis reactor and catalyst preparation reactor, and the post-reactor subsystem to condition the reactor outlet stream and analyze products.

Extraction of bio-oils and protein from biomass was explored using a novel solvent-based approach in the fourth subtask. The co-solvent system consisted of a hydrophilic ionic liquid and polar covalent molecule. Through direct transesterification, microalgal biomass yielded fatty acid methyl esters, and efforts continued in optimizing this process. Other efforts characterized how protein was partitioned in the co-solvent system.

Biochemical conversion of syngas into liquid fuels constituted the fifth subtask. Accomplishments included research results on mechanisms, kinetics, key enzymes, and the role of individual gases in the conversion process. Specific progress is presented in the production of liquid fuels from polyesters by methanolysis and thermal degradation.

The sixth subtask addressed biocontamination of alternative fuels. Accomplishments included enumeration of microbiological contaminants, description of a specific contaminated sample, isolation and characterization of microorganisms, measurement of degradation kinetics, and contaminant mediation and detection.

Biofuel corrosion research made up the seventh subtask. Work accomplished included a literature review with examination of case studies, establishment of a laboratory for study of microbiologically influenced corrosion, and results of preliminary laboratory experiments.

The final subtask focused on waste management using the HNEI patented Flash-Carbonization™ process for the production of biocarbons (charcoal). Efforts concentrated on modifications to the existing HNEI demonstration-scale Flash-Carbonization™ reactor and tests conducted with a laboratory-scale reactor. Many of these tests used Hawaii Kai sewage sludge as the feedstock. The Hawaii Kai sewage sludge has peculiar properties, perhaps due to additives employed by the Hawaii Kai treatment facility. Work focused on this feedstock and its carbonization behavior is continuing.

The task for Methane Hydrates activities comprised four subtasks: Hydrate Energy, Environmental Impacts of Methane Release from Seafloor Hydrates, Hydrate Engineering Applications, and International Collaborative R&D.

Our previous experimental and modeling activities focused on simple gas-water-hydrate systems. Natural hydrate deposits, however, occur in permafrost and seafloor sediments. Experiments were therefore initiated to investigate hydrate formation and destabilization in porous media. Quantities of two “standard” sands employed by the Japanese and U.S. national programs on methane hydrate R&D were obtained and employed in exploratory studies using the Raman calorimeter. The experiments validated the performance of that instrument when employed with sand-water-methane samples and provided preliminary data suggesting a significant impact of sand properties and “memory effects” on hydrate formation and dissociation.

The kinetic behavior of methane hydrate as it dissociates in the presence of thermodynamic inhibitors has been investigated experimentally in previous phases of the HEET initiative. Based on those results, we have proposed a mechanism where an inhibitor disrupts the dynamic equilibrium between hydrate formation and decomposition at the surface by binding up released water molecules and preventing them from re-crystallizing. During the present reporting period, we initiated additional experiments to test our hypothesis. The reagent of interest was glycerol ($C_3H_8O_3$), a triol having three hydroxyl groups. Glycerol appears to be an attractive alternative to alcohols or ethylene glycol, since it is inexpensive and relatively benign from a toxicity/environmental health perspective.

Microbial processes in the sediment and the water column are believed to play a major role in determining methane levels throughout the marine environment. The underlying metabolic pathways and the factors that affect these processes are not well understood and have been a focus area of the HNEI methane hydrate task. During the present phase of the HEET initiative, we participated in an oceanographic research cruise in the Beaufort Sea off the North Slope of Alaska, during which sediment samples were collected from shallow and cold water environments in methane-rich areas. Six of these samples were selected for long-term enrichment incubations and for DNA extraction. PCR amplification of the extracts indicate a diverse community of microorganisms associated with methane cycling including Type I methanotrophic bacteria, sulfate reducing microbes, and methanogens. Attempts to employ micro-calorimetry to observe quantifiable rates of microbial oxidation and reduction of methane in the most promising samples to date have not been successful.

As part of our goal to explore the use of gas hydrates for various engineering applications, we continued our investigation of hydrate H_2 storage. Although the extremely high pressures and low temperatures required to synthesize and maintain pure H_2 hydrate make it impractical as a medium to store and transport fuel, certain hydrate promoters such as tetrahydrofuran (THF) appear to show potential to stabilize the H_2 hydrate at less severe conditions. We were able successfully to synthesize both THF + H_2 and tetra-n-butylammonium bromide (TBAB) + H_2 hydrates using the Raman calorimeter and currently are pursuing development of both of these inhibitors.

Finally, for methane hydrates, as part of our goal to foster international collaborative R&D on methane hydrates, HNEI supported and helped to organize the 7th International Workshop on Methane Hydrate R&D that was held in Wellington, New Zealand in May 2012. A report on that workshop can be downloaded from the GNS Science website. During the present reporting period, planning also commenced for the 8th workshop that will be held in Sapporo, Japan at the end of May 2012. The Hokkaido branch of the National Institute of Advanced Industrial Science and Technology Science (AIST), an agency of the Government of Japan, is taking the lead for this workshop and HNEI will once again serve on the organizing committee and provide sponsorship.

Under the Alternate Energy Systems section, activities were completed for OTEC heat exchangers, storage analysis, and photovoltaic (PV) assessment. For the OTEC efforts, a heat exchanger performance testing facility was constructed, functional testing of an evaporator and condenser was completed, and a series of 6- to 18-month corrosion samples were removed from corrosion testing. The storage analysis work included scoping studies to determine battery size and operating characteristics, and siting studies to identify potential locations for battery system deployments. PV assessment activities encompassed the execution of a project plan including

planning, design, implementing, and managing tasks to fully instrument an existing grid-connected PV Inverter system on the Big Island of Hawai‘i.