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EXECUTIVE SUMMARY

This report summarizes work conducted under Grant Award Number N00014-17-1-2206, the Asia Pacific Research Initiative for Sustainable Energy Systems 2016 (APRISES16), funded by the Office of Naval Research (ONR) to the Hawai‘i Natural Energy Institute (HNEI) of the University of Hawai‘i at Mānoa (UH). The work conducted under APRISES16 comprises research, develop, testing, and evaluation (RDT&E) of a variety of distributed energy systems and novel energy technologies. APRISES16 also included significant effort directed toward power grid integration using Hawai‘i as a model for applicability throughout the Pacific Region. Areas of emerging energy technologies researched under APRISES16 included membrane-based energy systems (primarily fuel cells), battery systems, water and air filtration technology, hydrogen refueling technology, and novel printable photovoltaics. APRISES16 also included significant work in the area of biorenewable resources with activities in novel biocarbons, anaerobic digestion, and marine fuels; as well as continued work in the area of methane hydrates. Significant effort was also focused on alternative energy systems for electric power generation and integration into smart microgrids and energy efficiency technologies. Makai Ocean Engineering, under subcontract to the University of Hawai‘i, also continued their ongoing efforts to develop high-performance, low-cost heat exchangers. A brief summary of results by major task follows.

Task 1, Outreach and Program Management, supported senior faculty to provide overall program management and coordination, developed and monitored partner and subcontract agreements, and developed outreach materials for both technical and non-technical audiences. All subawardees completed the contracted work.

Task 2, Emerging Energy Technologies, included RDT&E in the areas of fuel cells, air and water purification technology, Li-ion batteries, hydrogen refueling infrastructure, and the development of new techniques for printable photovoltaic materials. Substantial progress was made in each of these areas.

Under APRISES16, HNEI continued its collaboration with the Naval Research Laboratory (NRL) supporting Northwest UAV (NWUAV), the licensee of NRL’s stamped metal bipolar plate unmanned aerial vehicles (UAV) fuel cell stack design, as they moved towards commercialization of their first generation 1.5 kW fuel cell power system. During this reporting period, HNEI
continued to provide troubleshooting support as NWUAV implemented their own production line for in-house stack builds based on the NRL fuel cell stack design.

HNEI also continued efforts to complete the move from the Hawai‘i Sustainable Energy Research Facility on Hawaiian Electric property to individual labs on the UH campus. With limited fuel cell test capability during this transition, efforts were focused on technology development, specifically novel transition metal-carbide catalysis and potentially lower cost electrolytes for vanadium flow batteries. During this period, HNEI developed a new electrochemical reduction method for production of high-concentration low-acidity vanadium electrolytes. Initial testing showed promising results.

In the area of Battery Energy Systems, HNEI, under this award, completed the characterization of Generation 2 commercial Li-ion titanate batteries under representative grid conditions, evaluated the impact on battery lifetime when electric vehicles (EV) batteries are used to support grid operation, progressed its models of battery packs lifetime performance including the impact of inhomogeneities in the batteries, and continued development of non-invasive characterization methodologies for Li-ion batteries. Testing was completed at HNEI’s Hawai‘i Sustainable Energy Research Facility prior to the move to campus. Key accomplishments are described in this report and in the 8 publications and 13 presentations resulting from the work.

Under Task 2, HNEI also progressed its work on filtration materials for those contaminants unable to be managed in-situ and for purification of water via forward osmosis (FO). Results include development of regenerative air filtration materials; fabrication of a test system for high-efficiency forward osmosis for water purification; and exploration of synthesis techniques for novel hybrid materials combining ionic liquids and ionic solids for high draw forward osmosis solutes. While the results from this study demonstrated the technical feasibility of photocatalytic regeneration of purification materials, results were not sufficiently promising to continue the effort under future awards. HNEI synthesized and characterized novel metallo-ionic liquids and molten salts using a syntheses strategy that combines ionic liquids and ionic solids presents opportunities to tailor the physico-chemical properties. Under future funding, we will optimize the FO system to enable accurate, long duration measurements and regeneration of draw solutes and evaluate commercial and HNEI-developed draw solutes for forward osmosis seawater desalination.

Task 2 also continued support for HNEI’s Hydrogen Refueling operations system at the Natural Energy Laboratory of Hawai‘i Authority (NELHA) fueling station site. Efforts included ongoing support for the commissioning of hydrogen production and compression equipment and hydrogen transport trailers. Finally, Task 2 also included a modest effort to continue the development of a novel low-cost printing process for the fabrication of electronic materials (primarily Cu2ZnSn(S,Se)4: CZTSSe) for solar energy conversion. While fully integrated solar cells made with this new technique reached power conversion efficiency up to 7%, the open circuit voltage of these cells was found to be approximately 250 mV lower than that typically measured on parent
chalcopyrite solar cells (e.g., CuInGaSe₂, CIGSe). Work was initiated to identify the causes of the lower than anticipated open-circuit voltage.

**Task 3**, Biorenewable Resources, continued research supporting the development of novel high-carbon products exhibiting characteristics of having undergone transient plastic phase during formation; continued efforts to identify commercial partners for HNEI’s novel anaerobic digestion technology; and continued the investigation into the storage and oxidation stabilities of DSH-76, CHCD-76, and their blends with F-76.

HNEI had previously reported that, using constant volume pyrolysis under moderate reactor conditions, the biomass feedstock is converted to a powdered, free-flowing biocarbon. During this period, a constant-volume reactor test bed was used to explore reaction conditions that resulted in biocarbons exhibiting characteristics of transient plastic phase during formation. Results from characterization of materials produced under this task resulted in a patent disclosure filed with the UH Office of Technology Transfer.

Under Subtask 3.2, a master design for the anaerobic system was completed to support transfer to industry. Efforts to identify a commercial partner for deployment have not, to date, been successful.

Under the third subtask, HNEI continued its investigation into the physicochemical properties and storage and oxidation stability of CHCD-76, SIP-76, and their blends with F-76. Under this award, two American Society of Testing and Materials (ASTM) methods, i.e. ASTM D4625 and ASTM D5304, were used to investigate the storage stability of these fuel samples. ASTM D5304 was also modified to determine the oxygen consumption rate of fuels. ASTM D2274 testing was conducted to study the fuel oxidation stability. Results are summarized in this report.

**Task 4**, Methane Hydrates, focused on three objectives: advancing our understanding of the environmental impacts of natural seeps and accidental releases of methane and other hydrocarbons in the deep ocean; exploring the feasibility of sequestering CO₂ in natural methane hydrate reservoirs; and continued promotion of international research collaborations on methane hydrates.

While previous research provided significant insight into the dissolution process of CH₄ bubbles in seawater, the majority of laboratory experiments have been performed using pure water and field studies have been conducted in seawater. Furthermore, laboratory experiments mainly focused on the effects of the hydrate film formation on the dissolving bubbles, and only a very small number of measurements have been made of the bubble dissolution rate under non-hydrate forming conditions. In consideration of these deficiencies, HNEI developed a facility and methods to measure the dissolution rate of CH₄ bubbles outside of the hydrate film forming regime. A description of the facility and preliminary data are reported.
Injection of CO₂ into methane hydrate reservoirs in sediment has been proposed as a means to destabilize the hydrate to release methane gas for energy, and to sequester CO₂ from the atmosphere. While the limited number of laboratory experiments suggests that the exchange proceeds too slowly to be viable at a commercial-scale, new theoretical thermodynamic analyses have indicated that gas mixtures of N₂ and CO₂ may improve the kinetics of replacement of CH₄ with CO₂ in hydrate deposits. In order to assess the feasibility of CO₂-CH₄ hydrate exchange for simultaneous methane production and carbon sequestration, experiments were performed. While the methane and CO₂ hydrate dissociation peaks were observationally separate, it was not easy to separate heat flows associated with each phenomenon. Further, the heat flows of methane hydrate dissociation were very irregular compared to previously performed methane dissociation experiments – possibly as a result of CO₂ hydrates forming concurrently with CH₄ hydrate dissociation. While this remains an area of interest, HNEI is unlikely to continue these efforts under future awards.

**Task 5,** Secure Microgrids, included a range of projects to develop, test, and integrate secure microgrid technologies into larger grid systems. Activities supported under this award included the Molokaʻi Dynamic Load Bank; a Bi-Directional EV Charging Demonstration Project; development of a Hawaiʻi Virtual Power Plant Demonstration; and the Coconut Island DC Microgrid.

In March 2015, Maui Electric Company, Ltd. (MECO) informed customers that the Molokaʻi grid had reached its system-level PV hosting capacity limit. In response, under previous APRISES awards, HNEI initiated a joint HNEI and MECO project, to deploy a custom controlled Dynamic Load Bank (DLB) as a practical, reliable, and inexpensive means to prevent the baseload diesel generators from operating below their minimum dispatch level, and enable the grid connection of significantly more rooftop PV on Molokaʻi island. In November 2018, following the load bank commissioning and implementation of the automated controls, the utility was able to add an additional 725 kW of distributed PV capacity to the system. Under APRISES15, HNEI and MECO conducted field tests to determine if the DLB was capable of meeting the demands of fast frequency response. Under APRISES16, this information was summarized and presented to MECO. While the capabilities of the DLB appear able to contribute in mitigating the impact severity of under-frequency events (e.g., avoid shedding a “kicker” load block in the Molokaʻi automatic under-frequency load shedding scheme), the existing BESS was delivering adequate grid-stabilizing dynamic response for effective system operation. It was determined that available engineering resources were inadequate to meet the substantial time and effort required to coordinate and tune the controls of the DLB with the existing fast-frequency responsive BESS on the island.

To tackle the complex optimization problem and demonstrate the use of bidirectional EV chargers, HNEI is developing and evaluating the performance of novel algorithms that optimize the
charge/discharge schedules of shared fleet EVs under its EV Bidirectional Charging demonstration project. The novel EV charger control algorithms are intended to ensure that the shared vehicles are efficiently assigned and readily available for transport needs while simultaneously, the controls deliver ancillary power and energy services through intelligent EV charge and discharge commands. Major project activities completed under APRISES16 included: finalizing electrical installation drawings; developing a bid package for the final construction and field installation work; awarding the construction contract to a contractor; installation and connection of the EV charger system; and continued development of the overall architecture of the proposed control algorithm. Under future APRISES funding, the web-based car reservation software will be finalized with the testing and evaluation phases initiated.

The objective of the Virtual Power Plant Demonstration project is to analyze the tradeoffs and demonstrate the economic dispatch of numerous customer- and utility-side energy/power services from multiple combined behind-the-meter (BTM) battery energy storage system plus photovoltaic (BESS + PV) units. Under APRISES14 and 15, a new electrical service was installed to connect the BESS units to the MECO power system, permits were acquired, and final site and equipment inspection was completed by MECO to allow installation of four Sunverge Solar Integration Systems. Ultimately, it was determined that the Sunverge rulesets were too limited to allow the full, dynamic economic optimization desired for the project. For this reason, under APRISES16, HNEI designed and implemented a web-based method to utilize the existing Sunverge website to allow external optimization algorithms and software to monitor and control the units. HNEI also contracted Haleakalā Solar to install a metering box using HNEI’s Advanced Realtime Grid Energy Monitor System (ARGEMS) to allow tests to begin. In a typical test scenario, HNEI plans to economically dispatch the four BESS + PV units according to the defined optimization problem and the time-varying load profiles of the four HVAC systems in conjunction with PV generation.

Coconut Island (Moku O Lo‘e) is a 28-acre (113,000 m²) island in Kāne‘ohe Bay off the island of O‘ahu and is home to the Hawai‘i Institute of Marine Biology (HIMB) of the University of Hawai‘i. As such, it is an ideal site for a renewable energy technology-based test bed, particularly representative of an isolated location vulnerable to energy disruption yet serving critical power needs essential to the research and educational mission of HIMB. The Coconut Island DC Microgrid Project was initiated under previous APRISES funding with the objective of demonstrating the performance and resilience of a DC microgrid designed to serve critical loads within two buildings on Coconut Island, including reliable power to critical loads during interruptions of grid supplied power, and providing the island with clean electrified transportation options powered primarily by the sun. With the major components procured under APRISES15, HNEI applied APRISES16 funding to procure the balance of the microgrid system components and infrastructure installation, including the construction and build-out of a control room next to one of the buildings. HNEI also installed the major components of the system within the control
room. Under future APRISES funding, HNEI will complete the installation and commissioning of the DC microgrid system and initiate the testing and evaluation phases of the research.

Task 6, Ocean Energy, supported two projects. Under subcontract to HNEI, Makai Ocean Engineering continued development of its thin foil heat exchangers; and in support of potential seawater air conditioning (SWAC) for Honolulu on the Island of O‘ahu, HNEI collaborated with the University of Hawai‘i’s Department of Oceanography to develop a thorough understanding of the baseline oceanographic conditions at the proposed site of the Honolulu SWAC system.

Makai Ocean Engineering has been developing Thin Foil Heat Exchangers (TFHX) for use in seawater-refrigerant, air-water, and water-water applications. In this report period, Makai advanced the TFHX design and, after resolving production issues, produced several full length plates; reduced both TFHX fabrication time and cost; and expanded TFHX pressure capacity and channel sizes and began geometric and mechanical characterization of the thermal, hydraulic, and structural/mechanical performance of these new combinations. This work added to Makai’s expertise in the fundamental principles of laser welding and furthered understanding of the TFHX technology. Additional detail is provided in this report and in Makai’s final report, available on the HNEI website.

The objective of the seawater air conditioning monitoring project, conducted in collaboration with the University of Hawai‘i’s Department of Oceanography, was to develop a thorough understanding of the baseline oceanographic conditions at the proposed site of the Honolulu SWAC system. At this time, the proposed SWAC plant for Honolulu will not be constructed as previously planned. Sampling and data collection for this SWAC monitoring project ended in December 2020.

Task 7, Energy Efficiency and Transportation included two activities in the area of energy efficiency and one focused on emissions from the conversion to electric vehicles. The two activities in energy efficiency were to support an efficient nano-scale microgrid at Ka Honua Momona (KHM), on Moloka‘i, Hawai‘i, a not-for-profit organization that supports the local Hawaiian community in Moloka‘i, including operation of aquaponics; and design and test an adaptive lighting study conducted in collaboration with the California Lighting Technology Center at the University of California, Davis.

Under previous APRISES awards, KHM collaborated with HNEI to develop an online dashboard providing visualization of the energy use and renewable energy production of their off-grid energy system for community education purposes. Under this award, the KHM compound was used as a proof-of-concept site to demonstrate a control scheme to optimize battery use, reduce inverter losses, and utilize energy that is otherwise wasted when a battery system can no longer store additional energy due to capacity constraints. HNEI’s objectives for this project were to develop a load shifting scheme to maximize utilization on a site whose load profiles have intermittent and
varying loads and finite battery storage capacity; increase system utility by adding load dumps ("opportunity loads") to utilize more available energy; and to test a “smart” predictive look ahead programming control strategy to match solar generation with partitioned battery storage in order to minimize inverter standby losses. The project successfully demonstrated that small off-grid renewable energy systems can significantly improve the utilization of the available energy sources (specifically, solar photovoltaic energy) by eliminating unnecessary inverter standby losses and adding opportunity loads to utilize excess available energy that may not otherwise be captured due to limited battery capacity. Details are provided in this report and the associated final report for the project.

In the second energy efficiency project, HNEI collaborated with the California Lighting Technology Center at the University of California, Davis to demonstrate and test a prototype adaptive lighting system intended to save energy and provide additional security in an outdoor setting. Demonstrations were established at the University of Hawaiʻi at Mānoa and at a civilian U.S. Navy facilities site. Significant energy efficiency gains were achieved at both sites and a number of recommendations for incorporation of adaptive lighting into real-world sites were put forward. A technical report describing the project details and key findings is available on the HNEI website.

The last activity under Task 7 was an analysis to assess the impact on fossil fuel use and emissions with the transition from Internal Combustion Engine (ICE) to plug-in Electric Vehicles (EVs), in combination with renewable electricity generation on a remote, isolated power grid. As expected, results show fossil fuel use and CO₂ emissions decrease with more clean power on the grid and decreasing ICE numbers. Results specific to varying charge scenarios was not explored but is included in other climate change related analysis being conducted by HNEI.

This final report describes the work that has been accomplished under each of these tasks, along with summaries of task efforts that are detailed in journal and other publications, including reports, conference proceedings, presentations, and patent applications. Publications produced through these efforts are linked below and available on HNEI’s website at https://www.hnei.hawaii.edu/publications/project-reports/aprises-16/.

**TASK 1: OUTREACH AND PROGRAM MANAGEMENT**

As the prime recipient of the agreement from ONR, HNEI conducts research, development, testing and evaluation across a range of alternative and enabling energy technologies; and is responsible for development and monitoring of partner and subcontract agreements. Under this task, senior HNEI staff developed and managed partner and subcontract agreements and coordinated development of outreach materials for both technical and non-technical audiences. Senior staff
also engaged directly with other DOD organizations, such as the Navy Facilities Engineering Command (NAVFAC) to assess energy needs of bases in the Asia Pacific region in an effort to continue to build these partnerships, with a focus on near-term opportunities for application of emerging energy technologies into Hawai‘i bases and elsewhere in the Asia Pacific region. Details of the various partner, subcontract, and outreach activities are included in the relevant task summaries organized consistent with the APRISES16 proposal, summarized below.

**TASK 2: EMERGING ENERGY TECHNOLOGIES**

Task 2 comprises five subtasks that included the development and testing of membrane-based energy systems (primarily fuel cells), evaluation and modeling of Li-ion batteries and battery systems, the development and testing of air and water filtration materials, support of the development and operation of hydrogen refueling infrastructure on the Big Island of Hawai‘i, and the development of novel thin film materials (primarily Cu$_2$ZnSn(S,Se)$_4$: CZTSSe) for solar energy conversion using inexpensive and scalable liquid-based processing. Details for each of these subtasks are described in more detail below.

### 2.1 Membrane-Based Energy Systems

Research in the area of membrane-based energy systems encompassed a range of activities. These included support of the Naval Research Laboratory’s (NRL) efforts to develop fuel cells for unmanned aerial vehicles and commercialize the technology with the licensee Northwest UAV and testing to evaluate the functionality of porous materials used by NRL to achieve high performance fuel cells; research to develop low cost and durable transition metal carbide catalysts applicable to fuel cells, water electrolyzers, and vanadium redox flow batteries; and a project to develop and demonstrate the applicability of high-concentration low-acidity salts to reduce the cost of vanadium flow battery technology.

Key accomplishment and details of the work conducted in each of these areas are described below. Associated publications and presentations are referenced at the end of this section.

**Support to NRL**

Under APRISES16, HNEI continued its collaboration with NRL supporting Northwest UAV (NWUAV), the licensee of NRL’s stamped metal bipolar plate unmanned aerial vehicles (UAV) fuel cell stack design, as they moved towards commercialization of their first generation 1.5 kW fuel cell power system [1]. Under APRISES15, HNEI led a one-week hands-on training course in
Honolulu for two engineers from Northwest UAV to support their efforts to develop in-house production, testing, and evaluation capabilities. HNEI continued this support under APRITIES16 through bi-weekly conference calls providing consultations regarding the design and development of the balance of plant components into a UAV chassis compatible system layout, and more importantly, review of fuel cell stack data and troubleshooting support as NWUAV implemented their own production line for in-house stack builds based on the NRL fuel cell stack design. As the work towards commercialization is not approved for public release, neither data or discussion of results is included in this report. For more information on the commercialization efforts of NRL and NWUAV, please contact Benjamin Gould at benjamin.gould@nrl.navy.mil.

As a follow-on to work published under APRITIES15 [2], HNEI supported NRL’s research efforts to better understand the role gas diffusion media (GDM) to actively control water management and enable high-power operation. GDM are an essential component of proton exchange membrane fuel cells (PEMFC), that mediate transport processes including electron and heat conduction, reactant gas diffusion and distribution to areas beneath the flow channel and land, and product water expulsion. Most PEMFC literature on gas diffusion media to date focuses on the influence of the cathode GDM with less emphasis of the role of the anode GDM. The goal of this effort was to maximize current densities over a broad range of operating conditions through effective water management implemented through GDM selection focused on both the anode and the cathode. The work demonstrated that tailored asymmetric pairings of GDMs on the anode and cathode can ensure adequate water expulsion from the cathode, lowering oxygen transport resistance, while maintaining adequate cell hydration leading to higher current densities vs. symmetrically paired GDMs. Under this collaboration, NRL performed fundamental fuel cell performance measurements, e.g. polarization and oxygen mass transport resistance experiments, along with more detailed measurements of GDM morphology through X-ray computed tomography and scanning electron microscopy. This work was correlated with net water drag/water balance measurements performed by HNEI. Net water drag (NWD) measurements [3,4] were performed using the same test cell and materials that NRL utilized. NWD represents the net water transport rate per proton transport through the membrane and is defined as the number of water molecules transported from the anode to cathode per hydrogen proton. The NWD can be calculated as the difference between the molar flow of water at the inlet vs. outlet for either the anode or the cathode \(n_{H2O}^{in}, n_{H2O}^{out}, n_{H2O}^{in}, n_{H2O}^{out}\) divided by two times the molar flow of water generated \(n_{H2O}^{gen}\) and can be derived independently from either side such that

\[
NWD = \frac{n_{H2O, a}^{out} - n_{H2O, a}^{in}}{2n_{H2O}^{gen}} = \frac{n_{H2O, c}^{out} - n_{H2O, c}^{in}}{2n_{H2O}^{gen}} [\text{Equation 1}]
\]

while satisfying the overall water balance within the cell as follows.

\[
n_{H2O, a}^{in} + n_{H2O, c}^{in} + n_{H2O}^{gen} = n_{H2O, a}^{out} + n_{H2O, c}^{out} [\text{Equation 2}]
\]
Positive values indicate a net water flux from the cell cathode to the anode, while negative values indicate net water flux from the cell anode. As water transport within the cell is a complex interplay of diffusion processes and electro-osmotic drag, practically speaking, the net water drag coefficient represents an indicator of the direction and fate of water generated in the cell. For all NWD results in this investigation, the percent difference in the water balance as described in Equation 2 were on average ±3.2% with a standard deviation of 1.2% validating the high fidelity of measurements performed at HNEI. NWD data was acquired during constant current experiments at 0.6 A/cm² and 1.5 A/cm², 80°C cell temperature, 150 kPaₐₐₜₜ outlet pressure, 2 stoich, and 25% and 50% RH on both the anode and the cathode. Following conditioning protocols, the current was stepwise ramped to the desired current density and allowed to stabilize for 2 hours prior to resetting the outlet water collection system. Due to the low water production rate of 10 cm² cells used in the experiments, water collection times at each point were no less than 16 hours to minimize errors in the water collection system. Figure 2.1.1 presents an example of results obtained at 50% and 25% relative humidity for select GDM material combinations, both symmetric and asymmetric. The data presented shows that the asymmetric combination of Freudenberg H23C3/H23C2 resulted in a higher net water drag from the anode to the cathode vs. the three symmetric pairs under all conditions with higher differences under wet conditions. The asymmetric combination also resulted in higher performance. One intriguing finding from this work was that the best performing cathode GDMs had variations in the pore morphology and shape of the pores, while the bulk porosity and average pore diameters did not change. Further details of this work will be reported in a peer-reviewed publication, which is being finalized for submission to the Advanced Functional Materials Wiley journal.

Figure 2.1.1. Exemplary net water drag coefficient measurements of selected anode and cathode GDM pairings at (A) 50% RHₐₐₜₜ and (B) 25% RHₐₜₜ. Positive values indicate a net water flux from the cell anode to the cathode, while negative values indicate net water flux from the cell cathode. Figure legend in (A) lists the anode and cathode GDM, respectively.
Under future APRISES awards, as described in the June 2021 APRISES17 progress report, HNEI intends to support NRL’s newest fuel cell development focused on producing new fuel cell architectures aimed at reducing overall system costs to support the Navy’s growing interest in the development of attritable technologies. Additionally, HNEI will continue work towards resuming full operation in the relocated on-campus laboratories.

**Transition Metal Carbide Catalysts**

Currently, Pt-group metals-based catalysts are used in most commercially available fuel cells and water electrolyzers. Unfortunately, they have the shortcomings of high cost, low earth abundance, and limited lifetime. The objective of this activity was the development of potentially low cost, active, and durable transition metal carbide catalysts for potential application to fuel cells, water electrolyzers, and vanadium redox flow batteries (VRFBs). While a variety of carbon-based materials have been widely investigated as electrodes for VRFBs, they often show limited activity and reversibility. Transition metal carbides are attractive candidates because they possess good electronic conductivity, low cost, high abundance, and outstanding thermal and chemical stabilities. The morphology of these transition metal carbide catalysts was designed to have a large active area to reduce kinetic voltage losses and a stronger bond between catalysts particles and support to delay degradation due to aging.

Vanadium carbide is of interest and investigated as catalysts for VRFBs because it possesses the same element, vanadium, as VRFBs, which would reduce potential contamination due to catalyst degradation. This work explored a simple and environmentally friendly synthesis process that involved in situ carburization of a metal precursor and a carbon material. Vanadium carbides was obtained from graphite (denoted VC\textsubscript{graphite}) and Vulcan XC72 (denoted VC\textsubscript{XC72}) as carbon sources and supports. Figure 2.1.2 shows the TEM images and the corresponding histograms of the particle size distribution of VC\textsubscript{graphite} and VC\textsubscript{XC72}. The vanadium carbides have a wide particle size distribution and a large particle size on the graphite support. In contrast, the vanadium carbide particles distributed on the XC72 support are smaller in size. These results show that VC\textsubscript{graphite} seems to agglomerate more than VC\textsubscript{XC72}. 
Figure 2.1. TEM images of (a) VC\textsubscript{graphite} and (b) VC\textsubscript{XC72}.

Figure 2.1.3 shows the baseline cyclic voltammetry curves for VC\textsubscript{graphite} and VC\textsubscript{XC72}. Graphite, the incumbent catalyst for VRFBs, was also included to benchmark the results obtained in this work. XC72 was also added because both carbon substrates are quite different and results were used to clarify the factors that influence the electrochemical activity of VC\textsubscript{graphite} and VC\textsubscript{XC72}. As shown in Figure 2.1.3a, the cathodic currents for all electrodes in 3 M H\textsubscript{2}SO\textsubscript{4} are due to the hydrogen evolution reaction. XC72 shows a higher cathodic current than other samples indicating that it is more active for the hydrogen evolution reaction. Although the cathodic current remarkably increases for graphite and XC72 in Figure 2.1.3b, a significant anodic current is not detected, indicating that the reversibility of the graphite and XC72 toward the V\textsuperscript{3+}/V\textsuperscript{2+} redox reactions is poor. In contrast, anodic and cathodic currents substantially increase on VC\textsubscript{graphite}, especially VC\textsubscript{XC72}, signifying an improvement in catalytic activity and reversibility toward the V\textsuperscript{3+}/V\textsuperscript{2+} redox reactions in comparison to graphite. The undesired hydrogen evolution reaction appears to have an important influence on the V\textsuperscript{3+} to V\textsuperscript{2+} reduction reaction. Figure 2.1.3c shows the catalytic activity of graphite, XC72, and vanadium carbides after background current subtraction. Anodic and cathodic currents substantially increase on vanadium carbides, signifying an improvement in catalytic activity toward the V\textsuperscript{3+}/V\textsuperscript{2+} redox reactions in comparison to graphite. The peak potential separation (\(\Delta E_p = E_{pa} - E_{pc}\)) and peak current ratio (\(I_{pa}/I_{pc}\)) indicate the reversibility of a redox couple. Values of 0.059 V for \(\Delta E_p\) and 1 for \(I_{pa}/I_{pc}\) at 25°C correspond to a reversible one-electron process (which is the ideal case) \([5]\). The vanadium carbide-modified electrodes exhibit lower \(\Delta E_p\) values, which are 0.16 and 0.13 V for VC\textsubscript{graphite} and VC\textsubscript{XC72}, respectively, than the pristine graphite and XC72 electrodes. The \(I_{pa}/I_{pc}\) for VC\textsubscript{XC72} (1.12) is closer to 1 than that for VC\textsubscript{graphite} (1.48), which also indicates enhanced reversibility.
Figure 2.1.3. Cyclic voltammograms on various electrodes (a) at 5 mV s\(^{-1}\) in N\(_2\)-saturated 3 M H\(_2\)SO\(_4\) at 25°C, (b) at 5 mV s\(^{-1}\) in N\(_2\)-saturated 3 M H\(_2\)SO\(_4\) + 1 M V\(^{3+}/V^{2+}\) at 25°C, and (c) the currents in Figure 2.1.3a were subtracted from those in Figure 2.1.3b.

In this work, vanadium carbides exhibited significantly enhanced catalytic activities and improved reversibility compared to graphite which is the incumbent catalyst for VRFBs. The improved performance of these promising materials has been evaluated by ex-situ cyclic voltammetry experiments. Future studies will include modifications to the catalyst synthesis approach to increase the activity by tuning the catalyst structure and morphology. The synthesis will then be adapted to integrate the new catalyst into an electrode for the fabrication of a VRFB single cell and validate its use in applications.

**Vanadium Flow Battery with High Concentration Electrolytes**

Under previous APRISEx funding, vanadium flow battery (VFB) work was initiated by HNEI with the objective to reduce battery cost by reducing salt purity and maximizing cell voltage efficiency. Under this award, a simple flow battery system with a 25 cm\(^2\) single cell and a titrator was fabricated and used for charging/discharging tests and to verify the electrolyte composition.
Electrolytes utilizing all four vanadium valences ($V^{2+}$, $V^{3+}$, $VO^{2+}$, and $VO_2^+$) were successfully prepared by conventional method with the high acidic vanadium electrolytes, and the effects of impurities on the $V^{2+}/V^{3+}$ and $VO^{2+}/VO_2^+$ redox reactions was investigated using rotating disk electrode analysis. The stabilities of all four electrolytes under low acid condition were investigated. With a concentration of 0.2 mol L$^{-1}$, V(II), V(III), and V(IV) electrolytes started precipitating at pH values of 4, 4.5 and 3.5, respectively; V(V) electrolyte kept clear till pH value up to 5 except of the color change from light yellow to light orange. The work indicated that all four vanadium electrolytes may be stable at low acid concentration down to mmol L$^{-1}$ grade.

Under APRISES16, HNEI also conducted research to improve the power and energy density, and reduce the corrosion impact on the system components by increasing the electrolyte concentration with low acid concentration for VFB. A new electrochemical reduction method was developed for producing the $V^{3+}$ solution. An in-situ pH, conductivity, and potentials monitoring system for both electrodes of a VFB was also established (Figure 2.1.4). Using this new method and the monitoring system, stable $V^{3+}$ solutions (2 mol L$^{-1}$ with pH 5-6 and ~5 mol L$^{-1}$ with pH 1-1.5) were successfully prepared. For the 3 mol L$^{-1}$ $VO^{2+}$ reduction, the final green solution was detected to be ~5.2 mol L$^{-1}$ of $V^{3+}$ with a little crystal precipitates. The V concentration increase was due to the solution evaporation. Figure 2.1.5 (a) and (b) shows the cell voltage responses under different current densities when the 2 and 3 mol L$^{-1}$ $VO^{2+}$ solutions were electrochemically reduced $V^{3+}$. The cell voltages linearly decreased with time under all current densities except the discharging at 30 mA cm$^{-2}$, which might be due to the initial electrode activation. Before the charge/discharge cycling test, a cell with the $V^{3+}$ solution in negative side and 2 or 3 mol L$^{-1}$ $VO^{2+}$ solution in positive side without acid had been completely charged to investigate the stability of $V^{2+}$ and $VO_2^+$ solutions. The results indicated negative electrolyte ($V^{2+}$, purples) was stable but positive electrolyte ($VO_2^+$, yellow) showed brown precipitates on pipeline when the cell was deeply charged. Fortunately, during the subsequent step discharges, the precipitates disappeared and negative electrolyte and positive electrolyte came back to clear green ($V^{3+}$) and blue ($VO_2^+$), respectively.
Figure 2.1.4. The in-situ pH, conductivity, and potentials monitor system for both electrodes of a vanadium flow battery.

Figure 2.1.5. The electrode potentials at different currents during the reduction of a) 2 and b) 3 mol L\(^{-1}\) VO\(^{2+}\) solutions.

Figure 2.1.6 shows the charge/discharge cycling data of a cell with 2 mol L\(^{-1}\) V solution (pH ~5) without acid under different current densities and different electrolyte cycling flowrates: a) 40 RPM; b) 100 RPM; and c) 100 RPM (last two charge/discharge cycles before positive electrode
clogging). The asymmetric results suggest reversibility issues which may come from the electrode activity or the electrolyte system. In Figure 2.1.6c, no charge/discharge at 60 mA cm\(^{-2}\) is due to the charging voltage reaches to the limit of 1.8 V, and also the clogging happened during the third discharge at 20 mA cm\(^{-2}\), which resulted in the cell failure.

![Figure 2.1.6](image)

Figure 2.1.6. The cycling charge/discharge of a cell with 2 mol L\(^{-1}\) V under different current densities and different electrolyte cycling flowrates: a) 40 RPM; b) 100 RPM; c) 100 RPM (last two charge/discharge cycles before positive electrode clogging).

Figure 2.1.7 shows the cell voltage responses to the initial separated a) charging and b) discharging tests with 3 mol L\(^{-1}\) V solution (pH ~1) without acid. There were brown precipitates in positive electrolyte pipeline during the charging at 20 mA cm\(^{-2}\). The instable voltage responses at last two charges (at 20 and 10 mA cm\(^{-2}\)) suggest that the clogging might happened in positive electrode. Same as the discharging of the cell with 2 mol L\(^{-1}\) V, the precipitates disappeared and negative electrolyte and positive electrolyte came back to clear green (V\(^{3+}\)) and blue (VO\(^{2+}\)), respectively after the step discharges in Figure 2.1.7b. The abnormal discharging behaviors at low current densities (20, 4 and 2 mA cm\(^{-2}\)) may suggest the dissolving processes of V(V) precipitates. Unfortunately, the membrane was noticed broken and positive electrolyte crossovers to negative
side after the step discharges. It might be a result of the V(V) precipitates clogging in positive electrode.

Figure 2.1.7. The cell voltage responses to the initial separated a) charging and b) discharging tests with 3 mol L$^{-1}$ V solution (pH ~1) without acid under different current densities in subsequence.

Figure 2.1.8. The ending colors of Vanadium electrolytes after applying, a) the new electrochemical reduction method; and b) fully charging with the VO$_2^+$ solution in positive side as a starting electrolyte; and c) discharging in Figure 2.1.6.
Under APRISES17, the novel reduction method for producing the $V^{3+}$ solution without acid may be filed to a patent. The reversibility issues will be figured out by the special electrochemical characterizations and attempted to be solved by modifying the membrane or the electrodes. The benefits of the vanadium flow battery system without acid may be demonstrated.

**Publications and Presentations**

*Peer-Reviewed Publications*


*Conference Proceedings and Presentations*


**References**


2.2 Battery Systems

The research conducted under subtask 2.2, Battery Systems, included four activities, (1) the completion of the characterization of Generation 2 commercial Li-ion titanate batteries under grid representative conditions, (2) the evaluation of electric vehicles (EV) batteries when used to support grid operation, (3) the development of battery packs lifetime performance models accommodating inhomogeneities, and (4) the development of non-invasive characterization methodologies for Li-ion batteries. Testing was conducted at HNEI’s Hawaiʻi Sustainable Energy Research Facility (HiSERF). Cell performance was modeled using tools developed under previous APRISES funding. Key accomplishments and details of the work conducted were all fully published and summarized below. The 8 publications and 13 presentations associated with this subtask are referenced at the end of this section.

Battery Durability under Power Systems Operation

The testing and analysis of the Generation (GEN) 2 Altairnano cells was completed and published under APRISES16 (Baure, 2020). The testing protocol for the cells was based on input from the utility company and lessons learned from the GEN1 cells. The commercial cells were tested under conditions representative of the various usages associated with modern grid applications as well as calendar aging. The cells exhibited remarkably small capacity loss after more than 450 days of cycle-aging testing. However, a careful analysis of the changes in their electrochemical behavior enabled the automatic quantification of the silent degradation modes, i.e. degradation that does not induce capacity loss, to forecast their impact over a 20-year lifespan (Figure 2.2.1). We showed that, for the cells tested at 35°C and held at low state of charge, capacity loss could accelerate after 6 years of deployment. Under all other conditions, if the temperature remained below 35°C, the capacity loss is limited and a 20-year deployment life should be attainable. These results provide confidence in the endurance of the two deployed MW systems using this battery technology on the island of Oʻahu and Molokaʻi. This study also demonstrated that the three main thermodynamic degradation modes were affected differently by the testing conditions and that their individual quantification is essential for accurate prognoses.
Durability of EV Batteries Used for Grid Services

Efforts to assess the durability of EV batteries under operations representative of providing grid services was completed under APRISES16 (Baure, 2019). This subtask started under APRISES12, where we showed negative impact to the batteries when using EV for energy shifting via vehicle to grid (V2G) usage. This was attributed to the additional usage of the cells. Additional work was undertaken under APRISES15 to assess that the impact of a different grid application, frequency regulation, on the same cells was lower on battery degradation. Under APRISES16, we addressed an additional important point for the battery community, whether the synthetic driving cycles often used to accelerate testing were representative of real driving (Figure 2.2.2). Based on the conventional metrics of capacity, resistance, and degradation, we found that although the synthetic cycles matched pretty well, the degradation mechanisms observed when batteries are tested under real constant driving cycles, the average current and charge capacity during discharge were important parameters to match the degradation extent. More importantly, it was found that traffic greatly influenced cell degradation and cycle life. Since none of the synthetic cycles sufficiently imitated the range of lifetimes and degradation profiles caused by real varied driving, we proposed that realistic EV battery testing must require looping several iterations of the same synthetic cycle at different intensities.
Battery Energy Storage System Modeling

Under APRISES16, the battery pack model developed under APRISES15 was used to investigate the variability of performance resulting from different levels of cell-to-cell variations (CtCV) at time of assembly (Dubarry, 2019). This study investigated the impact of several normally distributed intrinsic CtCV, individually or as a whole, on battery pack voltage response and capacity retention. It was found that, for all chemistries, CtCV do not significantly effect battery packs with batteries connected in parallel because of the possibility of self-balancing. When cells are connected in series, CtCV had much more of an impact on the assembly performance and that effect is chemistry dependent, NCA cells being the less affected.

The proposed methodology allowed investigating the relationship between cells quality and performance. Results showed that this is especially important for packs with cells connected in series (Figure 2.2.3). In view of a potential BMS implementation, nothing at the pack level was deemed accurate enough for automated estimation of the CtCV from the battery pack electrochemical response. At the single-cell level, the initial state of charge and capacity ration could be deciphered automatically at low rate but the accuracy of the estimation will drop with increasing rate because of the influences of the variations in resistance and rate capability.
Development of Non-Invasive Battery Characterization

Under APRISES16, we used the tools developed under previous APRISES awards to simulate the impact on temperature and current on the voltage response of the cell (Schindler, 2019), to investigate the application of our method on next-generation batteries (Anseán, 2020), and to help analyzing the impact of temperature gradients in collaboration with NRL (Carter, 2021).

In Schindler et al. (2019), we demonstrated how well change of kinetics could be simulated using the modeling framework developed under prior awards. As a showcase example, the incremental capacity characteristics of a typical high energy cell has been reconstructed at various temperatures and C-rates based on half-cell profiles recorded solely at ambient conditions. It has been shown that the intrinsic deviations of the kinetic behavior of the original and reconstructed cell can be sufficiently compensated by tuning the proposed kinetic model parameters. The parameter values show a well-defined, rate dependent Arrhenius behavior. By inter- and extrapolating the identified
Arrhenius correlations, a generalized emulation approach has been developed to predict the incremental capacity characteristics in a wide experimental parameter range while at the same time only relying on a minimal model (Figure 2.2.4). This is especially helpful for the application in battery management systems where only a limited amount of processing power is available.

In Anseán et al. (2020), we reported a framework to construct an accurate mechanistic model for a next-generation commercial representative Si–Gr//NMC811 battery. With new electrode configurations emerging in next-generation Li-ion batteries, it is important to provide adaptable, in-situ diagnosis and prognosis tools that have been proved successful in previous generation materials. The constructed model allowed us to emulate individual degradation rates of silicon and graphite within the blended negative electrode, that the battery could experience under real-life operating conditions. We proposed a series of key Features of Interest (FOIs) that are sensitive to degradation and must be analyzed in detail to understand and deconvolute concurrent aging modes (Figure 2.2.5). Due to the intrinsic nature of look-up tables, the features could be embedded on a microcontroller-based architecture.
In Carter et al. (2021), NRL assessed the influence of directionality of interelectrode thermal gradients on Li-ion electrochemical performance and safety. It was observed that, at ambient cell temperatures, the thermal gradient has no electrochemical effect, but that for a warmer cell, an interelectrode thermal gradient, regardless of its direction, accelerates capacity loss. HNEI was involved in comparing experimental incremental capacity data to simulated curves with specific degradation modes. We were able to diagnose that the directionality dictates which electrode is prone to failure (Figure 2.2.6): rapid negative electrode-centric degradation with extensive Li plating in the case of a colder negative electrode and warmer positive electrode, and gradual positive electrode centric degradation with a warmer negative electrode and colder positive electrode. These findings illustrate the sensitivity of warm Li-ion batteries to mild interelectrode thermal gradients, which become increasingly prevalent in multilayer packs and cylindrical cells where alternating thermal gradients are commonly observed and will likely lead to mixed modes of degradation.
In addition to the scientific research, we published one perspective paper (Dubarry, 2020) on battery state of health and one review paper (Barai, 2019) on non-invasive characterizations in collaboration with scientists from Argonne National Laboratory, the University of Warwick (UK), and Jaguar Land Rover.

**Publications and Presentations**

*Peer-Reviewed Publications*


**Conference Proceedings and Presentations**


2.3 Filtration Technology

Under Subtask 2.3, HNEI conducted research in three distinct areas; development of regenerative air filtration materials; development of a test system for high-efficiency forward osmosis for water purification; and exploration of synthesis techniques for novel hybrid materials combining ionic liquids and ionic solids for high draw forward osmosis solutes.

Regenerative Air Filtration Materials

This activity focused on developing a novel method for regenerating air filtration material through photocatalysis. The benefit of this technology would be to allow regeneration of air filtration materials used in fuel cells on site including shipboard or forward base applications.

In this effort, a novel surface treatment was developed to allow surface free radical generation under UV exposure. Titanium dioxide and graphene oxide was covalently bonded to the surface of granular activated carbon to form a uniform nano-scale coating using nitric acid pretreatment.
and a hydrothermal reaction. This combination of materials was hypothesized to utilize the free radical generating phenomenon of TiO$_2$ when it is exposed to UV radiation while utilizing graphene oxides’ ability to function as an electron sink for the TiO$_2$ generated electrons, preventing quick recombination, and thus allowing the free radicals to travel freely through the surface.

Coupling with graphene oxide has also been shown to activate TiO$_2$ under longer wavelengths of visible light. Graphene oxide was utilized in this study to enhance the efficiency of TiO$_2$ and to allow the free radicals produced under UV radiation to scavenge surface bonded air contaminants, in this case SO$_2$ molecules.

A custom air filtration test bed was used to expose air contaminated with SO$_2$ to the novel air filtration materials. The test bed allowed the characterization of the adsorption capacity of the novel air filtration materials. After adsorption capacity was determined, the material was submerged in an aqueous solution and exposed to UV radiation.

The preliminary results showed that the nanoparticle coating resulted in an approximately 46% decrease in adsorption capacity but was able to restore 87% of its initial capacity when regenerated for 20 hours. Hydrothermal synthesis of TiO$_2$/graphene oxide coated activated carbon was shown effective in producing a nanoscale, uniform coating of TiO$_2$ onto the surface of oxidized activated carbon. HNO$_3$ pretreatment was necessary to ensuring complete surface coverage by increasing the surface carboxyl groups on activated carbon. Presence of TiO$_2$ decreased the adsorption capacity of pure activated carbon from 0.139 to 0.075 g SO$_2$/g TiO$_2$/graphene oxide coated activated carbon, corresponding to a 46% drop.

Photocatalytic oxidation and water regeneration contributed to the overall regeneration of TiO$_2$/graphene oxide coated activated carbon. Water regeneration provided a significant effect where a 67% regeneration efficiency was obtained without any UV exposure. When exposed to UV light, an even higher regeneration efficiency of 87% was achieved and the respective photocatalytic mechanisms were speculated.

The results from this study demonstrate the technical feasibility of photocatalytic regeneration of purification materials.

**Forward Osmosis Apparatus**

Forward osmosis is a promising low pressure water purification technology with a low energy use potential. However, the widespread commercialization of forward osmosis technology is challenged by a lack of practical, cost competitive draw solute materials with high osmotic pressure and low reverse draw solute diffusion that can be efficiently separated from the desalinated water. Under APRlSES16, we initiated research on forward osmosis (FO) water purification technology with the intent of developing high-efficiency forward osmosis for water purification. The key accomplishments of this activity included (1) fabrication of a forward
osmosis water purification system to characterize the performance of forward osmosis draw solutions and membranes; (2) assessment and evaluation of current literature on forward osmosis water purification technology with emphases on FO draw solutions in order to develop an in-depth understanding of the physio-chemical attributes of ideal draw solutions; and (3) testing and benchmarking the performance of the FO system using commercial draw solutes.

Under APRISES16, a forward osmosis water purification testing system was fabricated to study the effects of draw solution properties, feed solution salt concentration, membrane quality, temperature and water flow rate on the efficiency of FO process, in terms of flux of the purified water and energy use of the system. The assembled forward osmosis system incorporates a forward osmosis membrane, a feed solution and draw solution tank assembly, a weighing balance, and two low pressure circulating pumps (Figure 2.3.1).

![Diagram of the forward osmosis water purification system.](image)

The FO system is a critical asset for HNEI’s future research on draw solutes and membrane materials development and testing. Procedures were developed for operating the fabricated FO system to ensure accuracy and reproducibility of experiments. Commercial concentrated draw solutions were prepared and utilized to develop protocols for benchmarking the performance of the FO system. Deionized water and high salinity sea water, were utilized as feed solutions in these studies. Three commercial inorganic draw solutes NaCl, NH₄Cl and KCl were selected at the concentrations of 0.6M, 1M, and 2M and tested with deionized water as feed solution, with a cellulose triacetate membrane.

Figure 2.3.2 illustrates the mass gain over time of the draw solutions from water permeating through the FO membrane from the deionized water feed solution. Figure 2.3.3 depicts the
resulting water flux from the FO process from the NH₄Cl draw solutions which are in the range of 6-12 L/m²·h.

![Weight increase comparison graph](image1)

Figure 2.3.2. Comparison of weight increase of all tested draw solutes with DI water feed.

![Water flux trends graph](image2)

Figure 2.3.3. Comparison of water flux trends of NH₄Cl solution using a feed solution of DI water.

As expected from osmotic pressure consideration of the solutions, generally the highest concentrated draw solutions (2M) performed better than 1M and 0.6M solutions, in terms of water recovery from the DI feed solution. The best draw solutions were tested against the practical feed solution, filtered Hawaiian island seawater, from Ala Moana beach. However, the water flux profiles were inconsistent with literature findings suggested the need for further improvement of the test apparatus prior to further performance testing of draw solutions or membranes.
These improvements, to be addressed with future funding include:

1) The automation of data (weight and time) collection to improve accuracy and enable longer experimentation times;
2) Weighing both the feed and draw solution tanks;
3) Integrating a draw solution/solute recovery unit into the FO system;
4) Re-assembling the FO system into a modular test stand on wheels for flexibility of use; and
5) Integrating energy use monitoring tools to enable the determination of the practical levels of renewable energy (e.g. photovoltaics), waste heat, or battery power that will be needed to run the FO system.

In future work, the FO system will be used to evaluate and compare the performance of HNEI developed draw solutions (including ionic liquid based draw solutions) against state of art draw solutions. Under APRISES16, we refined our syntheses and characterization methods of metallo-ionic liquids and molten salts to enable the quick translation of our synthesis expertise to the development of ionic liquid based FO draw solutions with high water flux, low toxicity, and easy regenerability. We finalized the characterizations of the HNEI developed iron metallo-ionic liquid, Fe₄(OAc)₁₀[EMIM]₂, through collaborations with Dr. Dera from Hawai‘i Institute of Geophysics and Planetology (HIGP), Dr. Leick from National Renewable Energy Laboratory, and Dr. Hagemann from University of Geneva.

**Forward Osmosis Solute Development**

In support of the development of high efficiency forward osmosis, HNEI characterized novel ionic liquids and molten salts with a high concentration of metal ions developed under previous awards. The physicochemical properties of the novel iron-based metallo-ionic liquid, Fe₄(OAc)₁₀[EMIM]₂, using various spectroscopic and thermal analyses techniques were successfully elucidated.

The materials development syntheses strategy of combining ionic liquids and ionic solids presents opportunities to tailor the physico-chemical properties of the resulting metallo ionic liquids and molten salts with unique properties. This approach can plausibly enhance or create new liquid salts with optimized properties for applications such as battery electrolytes and thermally or magnetically responsive, high flux draw solutes for forward osmosis water purification.

Conventional ionic liquids are salts with a melting temperature <100°C that usually contain large asymmetric organic cations and small inorganic anions with short-lived ion pairs. Ionic liquids are considered a class of “green compounds,” which are currently receiving a lot of interests in various fields [1-3]. Metal containing ionic liquids are a sub-class of ionic liquids that combine the properties of the traditional ionic liquids with the unique chemical and/or physical properties of the incorporated metals. The introduction of the metals greatly expands the possibilities of modification of the ionic liquids, enabling their varied use in interdisciplinary applications [4-7].
The high thermal stability, negligible vapor pressures and large liquidus range makes ionic liquids attractive for a wide range of uses including as catalysts, magnetic materials, electrolytes, and gas absorbers [8-10].

Ionic liquids have the potential to reversibly bind gases through a variety of intermolecular interactions [2,11-15]. 1-ethyl-3-methylimidazolium acetate, [EMIM][OAc], is one of the best known ionic liquids [2,16]. Mixtures of [EMIM][OAc] with inorganic salts have also been reported to form ionic liquid materials [17,18]. Following a similar approach, we have explored synthesis of other metal salts with [EMIM][OAc] in search of new metal containing ionic liquids and molten salts for battery electrolyte and, gas and water purification applications. We recently reported on the syntheses and characterization of the novel Mn$_4$(OAc)$_{10}$[EMIM], and Mn$_4$(OAc)$_{10}$[EMIM]$_2$·2H$_2$O compounds featuring extended chains of octahedrally coordinated Mn$^{2+}$ with all acetate ligands [7]. Under APRISE16, we successfully characterized the novel crystalline Fe$_4$(OAc)$_{10}$[EMIM], material that we developed. The material was characterized by X-ray diffraction (XRD), infrared vibrational spectroscopy (IR) and thermal analyses techniques, as discussed in detail below. A manuscript was published with three more under preparation on the synthesis, crystal structure, and properties of the novel materials.

Crystal Structure of Fe$_4$(OAc)$_{10}$[EMIM],: The X-ray studies of the synthesized materials were finalized using alternate funding in collaboration with Dr. Dera at HIGP. Figure 2.3.4. shows the crystal structure of the anhydrous Fe$_4$(OAc)$_{10}$[EMIM] and the hydrated Fe$_4$(OAc)$_{10}$[EMIM]$_2$·2H$_2$O metallo-ionic liquid compound developed at HNEI.

Figure 2.3.4. Crystal structures of Fe$_4$(OAc)$_{10}$[EMIM]$_2$·2H$_2$O (left) and Fe$_4$(OAc)$_{10}$[EMIM]$_2$ (right). EMIM ions are removed for clarity.
Figure 2.3.5 shows the topology of the anhydrous and hydrated Fe$_4$(OAc)$_{10}$[EMIM]$_2$ materials. The [EMIM] cation moieties do not participate in the coordination of the Fe ions, but are hydrogen bonded to the acetates.

![Diagram of Fe$_4$(OAc)$_{10}$[EMIM]$_2$](image1.png)

Figure 2.3.5. Schematic representation of the octahedral metal cation chain configuration in Fe$_4$(OAc)$_{10}$[EMIM]$_2$2H$_2$O and Fe$_4$(OAc)$_{10}$[EMIM]$_2$.

**Thermal Analyses of TGA and DTA Analyses:** Thermogravimetric analyses (TGA) and differential thermal analysis (DTA) were performed using a TA Instruments Q600 SDT employing a temperature ramp of 10°C/min and argon flow of 100 mL/min in-order to elucidate the thermal properties of the Fe$_4$(OAc)$_{10}$[EMIM]$_2$ on heat treatment from 50°C to 600°C. TGA indicates about 72 wt% mass loss of the material (Figure 2.3.6). The majority of the weight loss occurs in multiple overlapping steps in the 245-350°C temperature range. The TGA result supports the VT-IR analyses which suggests decomposition of the Fe$_4$(OAc)$_{10}$[EMIM]$_2$ complex upon heating to 280°C. The Fe$_4$(OAc)$_{10}$[EMIM]$_2$ is more thermally stable compared to [EMIM][OAc], but less stable than the iron acetate. The observed higher thermal stability of the Fe$_4$(OAc)$_{10}$[EMIM]$_2$ ionic liquid is likely due to increased lattice ordering and ionic bonding relative to [EMIM][OAc]. This high thermal stability was also observed previously with the Mn$_4$(OAc)$_{10}$[EMIM]$_2$ compounds [7].

![TGA and DTA curves](image2.png)

Figure 2.3.6. Thermogravimetric analyses (left) and Differential Scanning Calorimetry (right) of [EMIM][OAc], Fe(OAc)$_2$, and Fe$_4$(OAc)$_{10}$[EMIM]$_2$ at 10°C/min under Ar flow.
The DTA thermogram of Fe₄(OAc)₁₀[EMIM]₂ (Figure 2.3.6) illustrates four endothermic peaks with maximums at 108°C, 157, 296 (shoulder) and 324°C. The endothermic peaks at 296 and 324°C are attributed to the decomposition of the Fe₄(OAc)₁₀[EMIM]₂. The peak at 157°C is likely associated with structural rearrangement in Fe₄(OAc)₁₀[EMIM]₂. This thermal event is observed in VT-IR around 160-180°C as a disappearance of the vibrational peak at 755 cm⁻¹. The changing of the metal ion (size, type or charge) is envisioned to further alter the physicochemical properties of the metal containing ionic liquids resulting in new materials with unique properties for multiple applications.

*Temperature Programmed Desorption of Fe₄(OAc)₁₀[EMIM]₂:* The gas-phase products liberated during the temperature programmed desorption of Fe₄(OAc)₁₀[EMIM]₂ was monitored by means of quadrupole mass spectrometry (QMS) up to 450°C (Figure 2.3.7). The ions at m/z=15, 18, 28, 43, 45, 58, 74 were assigned to the molecules CH₃, H₂O, N₂ and CO, OC-CH₃, OH-CO, H₂C-CO-CH₃ and H₃CO-CO-CH₃, respectively. These m/z-values represent the key species involved in the thermal decomposition of Fe₄(OAc)₁₀[EMIM]₂. The decomposition pathway of the Fe₄(OAc)₁₀[EMIM]₂ involves four distinct regimes with peak temperatures of 88°C, 200°C, 267°C, and 345°C. The first regime is associated with the release of absorbed H₂O as observed by XRD in hydrated Fe₄(OAc)₁₀[EMIM]₂.
Infrared Vibrational Spectroscopy: IR spectra were recorded with a spectral resolution of 2 cm\(^{-1}\), with 30 or 64 scans in the range 600-4000 cm\(^{-1}\). The spectra were either recorded at 25°C in our lab with a Nicolet iS10 FTATR or with our collaborators at University of Geneva using variable temperature Biorad Excalibur Instrument equipped with a portable Specac Golden Gate heatable ATR setup, which allowed us to prepare samples in the glovebox. The FT-IR spectrum of Fe\(_4\)(OAc)\(_{10}\)[EMIM]\(_2\) is shown in Figure 2.3.8 compared with the spectra of the reactants; [EMIM][OAc] and Fe(OAc)\(_2\). The spectrum of the new Fe\(_4\)(OAc)\(_{10}\)[EMIM]\(_2\) compound shows the following frequencies at 755 cm\(^{-1}\) (CC stretching + OCO bending), 846 cm\(^{-1}\) (CC stretching + OCO bending), 944 cm\(^{-1}\) (CH\(_3\) bending), 1170 cm\(^{-1}\) (In plane C\(_{10b}\)H bending), 1042 cm\(^{-1}\) (CH\(_3\) bending), 1334 cm\(^{-1}\) (symmetric CO stretching), 1393 cm\(^{-1}\) (CH\(_3\) bending), 1568 and 1569 cm\(^{-1}\) (antisymmetric CO stretching), 613 and 644 cm\(^{-1}\) (OCO bending + CC stretching). The infrared modes of the ionic liquid [EMIM][OAc] and Fe(OAc)\(_2\) are in agreement with the literature.
Figure 2.3.8. Room temperature FTIR spectra of Fe$_4$(OAc)$_{10}$[EMIM]$_2$, Fe(OAc)$_2$ and [EMIM][OAc].

The Fe$_4$(OAc)$_{10}$[EMIM]$_2$ was further investigated by variable temperature FTIR to determine the effect of temperature on the molecular bonding and stability of the compound. Hence, the material was heated in the temperature range of 30-280°C with spectra collected at every 10°C interval. A phase transition of the compound is observed in the temperature range of 160-180°C, where the peak at 755 cm$^{-1}$ disappears, as well as the weaker bands at 670 and 710 cm$^{-1}$. Furthermore, the signals at 1334 and 1393 cm$^{-1}$ are merged into a broad peak, which may indicate the formation of a liquid phase of Fe$_4$(OAc)$_{10}$[EMIM]$_2$. These signals are attributed to the vibrational modes of the acetate ion, which might indicate that a change of the orientation of the acetate ion occurs leading to a lower interaction with the [EMIM]$^+$ before the onset of decomposition of the acetate.

Under future funding, we will re-fabricate and optimize the FO system to enable accurate, long duration measurements and regeneration of draw solutes. We will begin to evaluate commercial and HNEI developed draw solutes for forward osmosis seawater desalination, in terms of water flux, regenerability, and energy use.

Publications and Presentations

Peer-Reviewed Publications

References


2.4 Hydrogen Refueling Technology

The objective of this ongoing project is to evaluate the technical and financial performance of HNEI’s hydrogen refueling station and the technical performance of a fleet of three hydrogen Fuel Cell Electric Buses (FCEB) operated by the County of Hawai‘i Mass Transit Agency (MTA). The knowledge gained in this project will inform the MTA on benefits and issues associated with transitioning from a diesel bus fleet to a zero emissions FCEB fleet in support of the State of Hawai‘i’s and the County of Hawai‘i’s clean transportation goals.

Under APRIXES16 funding, HNEI supported the commissioning of the hydrogen station and development of procedures to manage the cost of hydrogen production; commissioning of the first MTA fuel cell electric bus; coordination with the County R&D department and MTA to develop
deployment concepts for three buses; and development of plans for installation of remote dispensing equipment at the MTA Hilo bus maintenance facility. Future work will include additional public outreach utilizing the NELHA hydrogen station and leveraging the opportunities provided by MTA bus operations; collecting and analyzing technical and economic performance data on bus and hydrogen station operations; and supporting work force development via training for bus operators and maintenance personnel.

**Hydrogen Station: Commissioning and Operational Costs**

Developed under funding from a variety of sources, including previous NRL and ONR awards, HNEI’s refueling station (Figure 2.4.1), located at the Natural Energy Laboratory Hawai‘i Authority (NELHA) on the Island of Hawai‘i is designed provide up to 65kg of hydrogen production per day. The dispensing system is designed to dispense hydrogen at 350 bar (5,000 psi).

![Figure 2.4.1. NELHA Hydrogen Production and Dispensing Station.](image)

As illustrated in Figure 2.4.2, fuel cell grade hydrogen produced at NELHA will be delivered to the MTA base yard in Hilo to support heavy-duty FCEBs operated by the MTA Hele-On public bus service. Three trailers (Figure 2.4.3) are available for transporting hydrogen between the production and fueling site. They are certified by the Federal Transit Administration for use on U.S. public roads. The hydrogen cylinders must be recertified every five years and have a legislated operational life of 15 years from their date of manufacture.
The station was fully commissioned in 2021 by HNEI and Powertech, the equipment supplier. The station uses a Proton Onsite (now NEL) electrolyzer to produce 65 kg of hydrogen per day at an outlet pressure of 30 bar (440) psi. A HydroPak compressor (Figure 2.4.4) compresses the hydrogen to 450 bar (6,600 psi).
The system is powered by the Hawai‘i Electric Light Company (HELCO) grid which includes approximately 60% renewable energy including solar, wind, and geothermal. The total power consumption of the hydrogen system including the electrolyzer, compressor and balance of plant is ~210 to 240 kW when operating at the maximum production rate of 65kg/day (2.7 kg/hr). This corresponds to approximately 78 to 88 kwh/kg of compressed hydrogen. The breakdown of the observed power usage is provided in Table 2.4.1.

Table 2.4.1: NELHA Hydrogen Station Observed Power Usage.

<table>
<thead>
<tr>
<th>NELHA Hydrogen Station Observed Power Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyzer in pre-start (no other equipment)</td>
</tr>
<tr>
<td>Electrolyzer in standby</td>
</tr>
<tr>
<td>Electrolyzer air cooler</td>
</tr>
<tr>
<td>Electrolyzer/Compressor room fans</td>
</tr>
<tr>
<td>Compressor Chiller</td>
</tr>
<tr>
<td>Electrolyzer filling/verifying A500 tank (air cooler)</td>
</tr>
<tr>
<td>Electrolyzer stack circulation state w/ air cooler</td>
</tr>
<tr>
<td>A500 filling with electrolyzer room fan/air cooler</td>
</tr>
<tr>
<td>Small compressor (only operates in short bursts)</td>
</tr>
<tr>
<td>Full production with fans, compressor, chillers:</td>
</tr>
</tbody>
</table>

This represents the largest single load on the NELHA research campus grid and has the potential to significantly increase electricity costs for the campus which is subject to energy and peak demand charges from HELCO. A study (Headley, 2020) was performed by Sandia National Laboratory to determine the cost of hydrogen production at the NELHA research campus given the rate structure options for the NELHA campus. The study determined that time-of-use energy charges could be beneficial, but the length of the low-cost energy windows and the specifics of the demand charges are important associated considerations as well. If the length of the low-cost window is not long enough to produce the daily hydrogen demand, or if the peak electricity demand charges do not also have a time-of-use component, time-of-use pricing may not be a good option. Also, pairing of flexible loads with other load centers is mutually beneficial with high levels of solar generation and optimal load scheduling using generation forecasting methods would be necessary to maximize value in this case. As regions increase their dependence on intermittent sources of generation, the value proposition of flexible hydrogen production will increase to improve the utilization of these resources. These research findings were published and are available on the HNEI website.

The dispensing system consists of a dispenser (Figure 2.4.5) connected to a Hydrogen Transport Trailer through a fueling post interface that is connected to the dispenser via an underground hydrogen piping distribution system. The hydrogen dispenser system is fully automated for unattended operation and programmed to “fail safe” by shutting spring loaded air-operated shut-off valves.
The fueling dispensers located at NELHA and at MTA are identical except for the addition of a novel boost compressor system at the MTA site integrated into the MTA fueling post (Figure 2.4.6). The boost compressor system was developed by HNEI and Powertech to dispense up to 90% of the hydrogen stored in the HTT in order to reduce transportation costs by not having to return half-filled HTTs to be refilled at NELHA.

The initial operations of this project, particularly operating in a corrosive salt air environment, have provided the opportunity for HNEI technical support staff to study and become familiar with
the hydrogen equipment and control systems and related maintenance challenges. Over time, this information will be transferred to the County MTA maintenance staff.

Commissioning the First MTA 21-Passenger Fuel Cell Electric Bus

The MTA (‘Hele-On’) 21-passenger FCEB (Figure 2.4.7) was purchased with State of Hawai‘i funds from the Energy Systems Development Special Fund. This bus, manufactured by Eldorado National, and converted to a hydrogen-electric drive train by U.S. Hybrid, is ADA-compliant and includes a wheelchair lift and spaces for two wheelchairs.

Onboard hydrogen is stored in composite carbon fiber cylinders located under the bus with a capacity of 19 kg. The fuel cell battery hybrid system is integrated with two 11 kWh Lithium-ion battery packs to provide motive power to a 200 kW electric drive system. At cruising speed, the fuel cell maintains the battery state of charge within a range that supports the long-term health of the battery. During deceleration, the electric motor acts as a generator sending power back into the battery (‘regenerative braking’). This contributes to overall system energy efficiency and improves bus mileage.

The bus fuel cell battery hybrid system was upgraded by replacing the original 30 kW fuel cell with a new state-of-the-art 40 kW U.S. Hybrid fuel cell. During commissioning trials, the fuel cell produced 46 kW, a 15% improvement. The range increased from 200 miles to 300 miles on flat ground with no passengers, a 50% improvement. The range is highly dependent on the route topography and driver skills. Due to weight issues discovered during commissioning trials, it was necessary to reduce the number of seats on the bus from its original 29 to 21 seats including the driver’s.

A U.S. Hybrid 10 kW bus export power system (Figure 2.4.8) was installed in the 21-passenger bus to enable the bus to provide 110/220VAC electric power at full power for up to 30 hours as
emergency power for civil defense resilience operations and humanitarian assistance when the grid power is down. The bus can be refueled in 10 minutes providing an additional 30 hours of emergency power.

![Figure 2.4.8. Bus Export Power System.](image)

**Deployment of Hele-On 19-Passenger Fuel Cell Electric Buses**

Two additional 19-passenger FCEBs (Figure 2.4.9) were acquired by the MTA from Hawai‘i Volanoes National Park (HAVO). These buses were converted by U.S. Hybrid and are of similar design to the 21-passenger FCEB. Onboard hydrogen capacity is 10 kg giving a maximum projected range of 150 miles. These buses are being upgraded with 40 kW U.S. Hybrid fuel cells and A123 Lithium-ion batteries using $245,000 of funding provided by the County of Hawai‘i.

![Figure 2.4.9. HAVO 19-Passenger FCEB.](image)
Figure 2.4.10 is a conceptual design of the hydrogen fueling dispensing system located at the MTA base yard in Hilo comprised of never used repurposed new equipment that was originally intended to support two buses at Hawai‘i Volcanoes National Park.

![Figure 2.4.10. MTA Fueling Dispensing Station.](image)

HNEI consulted with the MTA to select the location illustrated in Figure 2.4.11 for the hydrogen dispensing system. This single dispenser could support approximately 22 buses (illustrated) over a 6-hour period at a 16-minute fueling interval.

![Figure 2.4.11. MTA Site with Fueling Dispenser.](image)

In addition to the technical and cost analysis, HNEI is coordinating with the University of Hawai‘i’s Hawai‘i Community College, the County of Hawai‘i MTA, U.S. Hybrid, and bus operator
contractor Roberts Hawai‘i to support the introduction of workforce development programs to train drivers and technicians on hydrogen safety and to operate and service the FCEBs and other battery electric vehicles.

This project has made a critical contribution to the implementation of the County of Hawai‘i’s hydrogen economy vision as illustrated in Figure 2.4.12. The County is positioned to leverage this project to attract additional funding from the Biden Administration’s “Hydrogen Hub” program to support the execution of its vision and was one of two organizations invited to present their visions at the Hydrogen Shot Summit in October 2021.

![Figure 2.4.12. County of Hawai‘i Closed Loop Hydrogen Economy Vision.](image)

**Publications and Presentations**

**Peer-Reviewed Publications**

2.5 Printable Photovoltaics

The overall goal of this task is to develop thin film materials for photovoltaic applications using low-cost, scalable “printing” processing. This task continues work initiated under previous ONR-funded efforts to develop novel thin film materials (primarily Cu$_2$ZnSn(S,Se)$_4$: CZTSSe) for solar energy conversion using cheap and scalable liquid-based processing. Printable inks containing all the necessary components to form the solar absorber have been developed. These inks can be used to coat substrates using high-throughput techniques, such as spin coating and inkjet printing.

Under APRIS12 funding, a technology to form CZTSSe thin films using nano-crystalline “inks” made of CZTS (sulfide) nanoparticles with controlled composition, size, and morphology was developed. Printed inks were subsequently heated with elemental selenium to form polycrystalline CZTSSe absorbers with power conversion efficiency (PCE) of approximately 2.3% (as measured
with fully integrated CZTSSe-based solar cells). Although promising, this technique was not reproducible, as nanoparticles tend to agglomerate quickly in our inks after initial dispersion, making the printing step difficult. Under APRISES14, nanoparticle-based inks were replaced with ones containing only molecular complexes of copper, zinc, and tin (SnCl₂, CuCl and ZnCl₂) and thiourea (sulfur source) dissolved in methanol (Figure 2.5.1a). The resulting CZTS solutions are very stable and easy to process. After heating under selenium atmosphere, CZTS ink is converted into CZTSSe absorbers with exceptional crystallinity and void-free (Figure 2.5.1b). Fully integrated solar cells made with this new technique reached power conversion efficiency up to 7% (Figure 2.5.1c). However, the open circuit voltage ($V_{OC} = 400$ mV) measured on ZTSSe cells was found to be approximately 250 mV lower than that typically measured on parent chalcopyrite solar cells (e.g., CuInGaSe₂, CIGSe).

![Figure 2.5.1.](image)

Figure 2.5.1. (a) Picture of a stable molecular ink containing metal chlorides, thiourea and methanol. (b) Scanning electron microscopy cross-sectional view (colored image) and (c) current-voltage characteristic of a printed CZTSSe solar cell.

Under APRISES16, solid-state properties of CZTSSe solar cells were further analyzed to identify the origin of the lower than expected voltage. Temperature-dependent current-voltage (J-V-T) characteristics were measured from room temperature down to 150K using a cryostat cooled with liquid-He and equipped with a temperature controller (Figure 2.5.2a). Devices were illuminated using a white LED lamp which illumination (1 sun) was adjusted until the devices short-circuit current density matched that measured with the 1000W solar simulator. Finally, cells open circuit voltage ($V_{OC}$) were extracted from the J-V-T characteristics and plotted as function of temperature. The $V_{OC}$-T characteristic presented in Figure 2.5.2b provides important information regarding the dominant recombination path in the solar cell. In the absence of defects at the cell’s top interface, as seen with high efficiency CuInGaSe₂ (CIGSe) cells for example, the extrapolation of the characteristic to 0K would yield an activation energy $E_A$ equal to the solar absorber’s bandgap, implying recombination happens primarily in the semiconductor’s bulk. In contrast, the extrapolation of the $V_{OC}$-T characteristic measured on the CZTSSe cells reveals an activation energy (787 meV) significantly lower than the absorber’s bandgap (1,100 meV). Such large disparity between $E_G$ and $E_A$ can be explained wither by a defective interface and/or non-ideal alignment of energy bands at the CdS/CZTSSe heterojunction (a “cliff-like” conduction band
Another fundamental difference observed between our CZTSSe cells and high efficiency CIGSe is the saturation open circuit voltage ($V_{\text{SAT}}$), a parameter representing the maximum quasi-Fermi level split (QFLS) achievable before freeze-out of the recombination mechanism dominating at room temperature. For CIGSe, $V_{\text{SAT}}$ is typically achieved at 90K, with a value (990 mV) corresponding roughly to 75% of the bandgap gap value. In contrast, $V_{\text{SAT}}$ measured on CZTSe (550 mV) represents only 50% of the bandgap and is achieved at a much higher temperature (175K), suggesting possible “pinning” of the Fermi level at the hetero-interface.

![Figure 2.5.2](image.png)

Figure 2.5.2. (a) Picture of the experimental setup used to measure the activation energy of main recombination mechanism in a solar cell and (b) Open circuit voltage versus temperature curve measured on a CZTSSe solar cell.

Surface passivation strategies were evaluated as means to heal CZTSSe interfacial defects and reduce the voltage deficit. Reports showed that doping chalcopyrite (CIGSe) absorbers with alkali, such as sodium, can enhance electronic properties and improve $V_{\text{OC}}$. In a typical CIGSe thin film synthesis (co-evaporation over Mo-coated soda lime glass, SLG), sodium naturally present in SLG diffuses through the Mo layer and passivates defects in the absorber, however, work published by Repins et al. [1] showed that the out diffusion of Na from the SLG during growth of CZTSe is not sufficient to achieve good solid-state properties. Based on these results, our group evaluated methods to supply sodium ex-situ by evaporating a 50 nm thick NaF layer directly at the surface of CZTSSe sample. The solid-state properties of representative untreated and Na-F treated CZTSSe are summarized in Table 2.5.1. On average, Na-doping did not seem to have improved CZTSSe solar cells since untreated samples exhibited higher $V_{\text{OC}}$ compared to NaF-treated ones. It should be noted that the overall performances of the samples used for this experiment were low, as highlighted by the efficiency of the baseline (1.62% vs. 7% for cells from other batches). Nonetheless, results suggest NaF deposition after absorber growth does not lead to any appreciable improvements on solid state properties. Recent work reported by our team concluded that supplying sodium prior absorber growth, for example by depositing NaF directly onto the substrate, is more effective in passivating both bulk and surface defects [2].
### Table 2.5.1. Solid state properties of bare and NaF treated CZTSSe solar cells.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voc [mV]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Eff [%]</th>
<th>Rs [Ω/cm²]</th>
<th>Rsh [Ω/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated CZTSSe sample</td>
<td>292.6</td>
<td>18.84</td>
<td>31.23</td>
<td>1.62</td>
<td>9.93</td>
<td>35.69</td>
</tr>
<tr>
<td>NaF treated CZTSSe sample</td>
<td>176.42</td>
<td>21.98</td>
<td>28.44</td>
<td>1.17</td>
<td>3.61</td>
<td>16.0</td>
</tr>
</tbody>
</table>

### References


### TASK 3: BIORENEWABLE RESOURCES

Under Task 3, Biorenewable Resources, HNEI worked in three distinct areas. Based on work conducted under previous awards, HNEI continued to explore conditions in a constant volume reactor that resulted in the production of biocarbons exhibiting characteristics consistent with having undergone a transient plastic phase. Under Subtask 3.2, a master design for the anaerobic system was completed to support transfer to industry. Under the third subtask, HNEI continued its efforts to characterize the physicochemical properties and storage and oxidation stability of CHCD-76, SIP-76, and their blends with F-76. Various American Society of Testing and Materials (ASTM) methods were used to investigate both the storage stability and fuel oxidation stability of the fuels. Results are summarized in this report.

### 3.1 Novel Biocarbons from Biomass

Biomass can be a renewable resource for the production of energy, fuels, chemicals, and materials. The production of biocarbons with high, fixed-carbon content has been a research focus under earlier APRISES awards. Exploring the conversion of biomass under constant-volume reactor conditions resulted in the production of biocarbons that exhibit characteristics consistent with having undergone a transient plastic phase (TPP) (Figure 3.1.1). Under less severe reactor...
conditions, the same biomass feedstock is converted to a powdered, free-flowing, biocarbon. Yields of these unique and novel biocarbons from constant volume pyrolysis and their fixed carbon contents have proven to exceed those previously reported in the literature using conventional carbonization methods and less developed techniques such as hydrothermal carbonization. This task used a constant-volume reactor test bed to explore reactor conditions that resulted in TPP biocarbon formation. Results from characterization of materials produced under this task resulted in a patent disclosure filed with the UH Office of Technology Transfer. Additional details will be provided by publication of results when intellectual property protection has been completed. Articles in the archival literature will be available on HNEI’s website upon publication.

![Figure 3.1.1. Transient plastic-phase biocarbon.](image)

### 3.2 High-Rate Anaerobic Digestion

This objective of this subtask was to develop system design and life cycle costing of high-rate anaerobic digesters for use as point source processing units that produce reuse water and energy rich biogas and to seek a commercial partner for future deployment.

Under APRISE16, a master design was developed, inclusive of PID diagrams, costing, manufacturing, and shipping to build and install a wastewater treatment system designed from past research. PID diagrams were constructed that considered targeted organic loading rates and hydraulic retention times. The system was shown to process contaminants of emerging concern and more efficient reductions of estrogens than previously reported.

Efforts to identify a commercial partner for deployment has not, to date, been successful.
3.3 Marine Fuels

Non-ester renewable fuel (NERF) is a class of biofuels comprising pure hydrocarbons that are indistinguishable from their petroleum counterparts. NERFs have many advantages over bioethanol and biodiesel, e.g. higher energy content, better low temperature quality, and superior stability and material compatibility [1]. NERFs are also interchangeable with petroleum diesel in the existing fuel distribution and diesel engine infrastructure. As such, NERFs are more likely to meet the specifications of alternative fuels. NERFs, such as hydroprocessed renewable diesel (HRD-76), catalytic hydrothermal conversion diesel (CHCD-76), and synthesized isoparaffin (SIP-76), also known as direct sugar to hydrocarbon (DSH-76), have been produced in sufficient quantity for testing by the U.S. Navy as drop-in replacement for NATO F-76.

Although blends of HRD-76, CHCD-76, SIP-76, and conventional F-76 have already been used to power Navy surface ships [2], the physicochemical properties and storage and oxidation stability of CHCD-76, SIP-76, and their blends with F-76 haven’t been thoroughly investigated. In the present study, two American Society of Testing and Materials (ASTM) methods, i.e. ASTM D4625 [3] and ASTM D5304 [4], were used to investigate the storage stability of these fuel samples. ASTM D5304 was also modified to determine the oxygen consumption rate of fuels. ASTM D2274 testing [5] was conducted to study the fuel oxidation stability.

Petroleum F-76, SIP-76 and CHCD-76 were provided by the Naval Fuels and Lubricants Cross Function Team at Patuxent River, Maryland, United States (PAX River). The SIP-76 and CHCD-76 fuel lots were synthesized by Amyris Biotechnologies and Applied Research Associates, respectively. The petroleum F-76 was refined by CITGO Petroleum Corporation. The fuels were used as received, unless otherwise noted. Methods for physicochemical property measurements have been reported elsewhere [6-8].

Results of the storage stability and oxidative stability test campaigns are summarized below.

Storage Stability

Fuel storage stability is highly affected by fuel composition, especially the content of aromatics, sulfur, and oxygenated compounds. Both the long-term ASTM D4625 and the accelerated ASTM D5304 methods were employed for storage stability testing. As CHCD-76 can be used in neat form and SIP-76 is typically blended with F-76, CHCD-76, SIP-76, and a 50/50 blend of SIP-76 and F-76 were selected for ASTM D4625 tests. Figure 3.4.1 displays the amount of insolubles formed after each test period. The values shown are the average of three samples obtained by the same operator with the same apparatus under constant operating conditions on identical test material. The F-76 data were obtained in previous study [6]. The amount of total insolubles formed in SIP-76 is lower than that formed in F-76 samples, demonstrating that SIP-76 is more stable than petroleum F-76 and contains less unstable precursors, which is consistent with the
composition analysis. The fuel storage stability of F-76, therefore, could possibly be improved by blending with SIP-76, as illustrated by the results obtained for 50/50 blends of SIP-76 and F-76 after 24 weeks of storage. Similar to SIP-76, CHCD-76 also possessed superior storage stability compared with F-76. Although the amount of insolubles formed in F-76 is significantly higher than that in SIP-76 and CHCD-76, the total insolubles formed in F-76 over the whole storage period are lower than the maximal allowed amount (3 mg/100mL) specified in the MIL-DTL-16884N. These are based on 16 hour ASTM D5304 tests, for which 16 hour ASTM D5304 tests yields approximately the same amount of insolubles as 20°C storage for 27 months under atmospheric air pressure [4], and the total amount of insolubles formed after 24 weeks, 0.53 mg/100mL, is about 6 times lower than that specified. In addition, the amount of filterable insolubles formed in these three fuel samples are less than the adherent insolubles formed in these samples. As a result of the low amounts of insolubles formed, no significant linear relationships were found between the storage time and the amounts of filterable or adherent insolubles formed in SIP-76 and CHCD-76.

The influence of long-term storage on fuel physicochemical properties was also investigated in this study. Figure 3.4.2 (a) and (b) displays the change of fuel kinematic viscosity and density during the 24 week test period. The viscosity and kinematic viscosity of the fuels stay almost constant during the 24 week storage period. As with the insoluble formation, no direct relationships were found between the storage time and change of fuel kinematic viscosity and density. The results indicate that the long-term storage has more impacts on the PV and AN of the fuel sample, especially the PV. The PV of SIP-76 and CHCD-76 increased about 4 and 7 times, respectively.
Figure 3.4.2. Change of fuel kinematic viscosity at 40°C (a) and density at 15°C (b) after ASTM D4625 test.

The oxygen overpressure method, ASTM D5304, was also employed to study the storage stability of the fuel samples. The advantages of this test method compared to ASTM D4625 is the greatly reduced testing time, 16 hours vs. 24 weeks, and reduced sample size, 100 mL vs. 400 mL. As mentioned above, the 16 hour ASTM D5304 test yields approximately the same amount of insolubles as a 27 month storage test using air at atmospheric pressure at 20°C [4]. Figure 3.4.3 (a) and (b) shows the insolubles formed in the neat and blended fuel samples after 16 and 40 h tests. As expected, the amount of insolubles formed in the F-76 samples is higher than that in SIP-76 and CHCD-76 samples, indicating that these two biofuels are more stable compared with petroleum F-76. This is consistent with the ASTM D4625 test results. In contrast with the ASTM D4625 tests, the amount of filterable insolubles formed after ASTM D5304 tests is usually higher than that of adherent insolubles. After the 16 hour tests, the amount of filterable insolubles formed usually increases with the F-76 composition, whereas no significant relationships were observed between the adherent insolubles formation and F-76 content. However, as with filterable insolubles, the amount of adherent insolubles formed increased with the F-76 composition after 40h tests. The insoluble formation is also related to the test period, and the longer test period induces more insoluble formation. It should also be noted that the insoluble formation in all the neat and blended fuels investigated fall below the MIL-DTL-16884N specification, < 3.0 mg/100mL.
Figure 3.4.3. Insolubles formed in SIP-76, CHCD-76 and their blends with F-76 determined by 16 hour (a) and 40 hour (b) ASTM D5304 tests. F, A, and T represent filterable, adherent, and total insolubles, respectively.

The ASTM D5304 test results appear consistent with those obtained from ASTM D4625. SIP-76 and CHCD-76 were more stable after long-term storage compared to petroleum F-76 and this is consistent with their lower content of unstable precursors. Blending SIP-76 and/or CHCD-76 with F-76 would improve the fuel storage stability. In addition, the insoluble formation mechanism is different under conditions for ASTM D4625 and D5304 tests. The ASTM D4625 test induced the formation of more adherent insolubles, while more filterable insolubles were formed during ASTM D5304 tests. Selected physicochemical properties of SIP-76, CHCD-76 and their blends were different after the long-term storage; changes of PV and AN were significant, whereas kinematic viscosity, density and HHV were not. Overall, the long-term storage had greater impact on the PV, for example, the PV of F-76 increased approximately three and five times, respectively, after 16 and 40 h ASTM D5304 oxidation tests.

Oxidation Stability

Although the ASTM D5304 method was initially developed to measure insoluble formation in fuel samples under stressed conditions, (i.e. 90°C and pure oxygen at 800 kPa), it can also be utilized to investigate the oxidation process by characterizing the oxygen consumption of the fuel samples. This entails monitoring the pressure in the vessel and calculating the percentage of oxygen remaining. Figure 3.4.4 compares the oxygen consumption of SIP-76 and CHCD-76 with F-76 after 16-hour ASTM D5304 tests. The oxygen consumption of the fuel samples is comparably rapid at the initial stage of the 16-hour test period owing to the oxidation of unstable precursors.
As the precursors become fully reacted, the consumption rate slows. The oxygen consumption rate is reflected by the slope of the linear regression curve shown in the figure. The lower oxygen consumption rate of SIP-76 compared to F-76 and CHCD-76 indicates that SIP-76 is more stable and this is consistent with the results obtained from ASTM D4625 tests. The slightly higher oxygen consumption rate of CHCD-76 compared to F-76 is noteworthy, given the latter’s higher insoluble concentrations (Figure 3.4.4). This may result from the oxidation of unstable precursors under conditions of high temperature and pressure, but without oxidized products that necessarily form insolubles. Figure 3.4.4 also presents data reflecting the oxidation process of the fuel blends. As noted earlier, the oxygen consumption rate of CHCD-76 is faster than that of F-76 and the oxygen consumption rate of a 50/50 CHCD-76/F-76 blend lies between them. The oxygen consumption rate of 50/50 SIP-76/F-76, however, is lower than that of SIP-76.

![Oxygen consumption of SIP-76, CHCD-76 and their blends with F-76 under modified ASTM D5304 test conditions.](image)

The accelerated ASTM D2274 is a standard method for the testing of oxidation stability of middle distillate petroleum fuels and biofuels. This method was employed to investigate the oxidation stability of SIP-76, CHCD-76, and their blends with petroleum F-76. Although the ASTM D2274 method only requires a 16 hour test period, MIL-DTL-16884N requires a 40 hour oxidation period using the same apparatus and limits total insolubles formation to < 1.5 mg/100 mL for F-76 and its blends. The insoluble formation in SIP-76, CHCD-76, and their blends with F-76 was determined for 16 and 40 hours (Figure 3.4.5 (a) and (b)), and the results were compared to that of F-76 published previously [6]. As with ASTM D5304 tests, the insoluble formation is correlated to the fuel composition and test period. The oxidation of F-76 produces more insolubles and higher F-76 blends result in the formation of more insolubles. The total amount of insolubles formed in
fuel samples after 16 hour tests are all lower than the corresponding samples after 40 hour tests. The insoluble formation after 40 hour tests, however, is mainly contributed by the formation of adherent insolubles, which is different from the test results from ASTM D5304, but consistent with those from ASTM D4625. This demonstrates that increased pressure will accelerate the formation of filterable insolubles, as the ASTM D2274 test condition is similar to that of ASTM D5304 except for the higher O₂ pressure, 800 kPa. Note that the insolubes formed in F-76 samples (40 h D2274) approach the limit of the MIL-DTL-16884L specification.

Figure 3.4.5. Insolubles formed in SIP-76, CHCD-76 and their blends with F-76 determined by 16 hour (a) and 40 hour (b) ASTM D2274 tests.

In summary, SIP-76 possesses better oxidative stability compared with petroleum fuel F-76, whereas CHCD-76 exhibited slightly higher oxygen consumption rate in comparison with F-76. The increased content of the SIP-76 and CHCD-76 in the fuel blends generally decreases the insoluble formation and increases the oxidation stability of the fuel samples. The increased pressure during the oxidation process would accelerate the formation of filterable insolubles by comparing the type and amount of insoluble formation in ASTM D2274 and D5304 tests.

References


**TASK 4: METHANE HYDRATES**

National R&D programs on methane hydrates were initiated in Japan and India in the mid-1990’s with the goal of commercial gas production within a twenty-year time horizon [1]. The U.S. established its own program in May 2000. The Methane Hydrate Research and Development Act of 2000 (Public Law 106-193) included seven technical areas of focus: (1) identification, exploration, assessment, and development of methane hydrate as a source of energy; (2) technology development for efficient and environmentally sound recovery of methane from hydrates; (3) transport and storage of methane produced from methane hydrates; (4) education and training related to methane hydrate resource R&D; (5) assessment and mitigation of environmental impacts of natural and purposeful hydrate degassing; (6) development of technologies to reduce the risks of drilling through methane hydrates; and (7) support of exploratory drilling projects.

The objectives of the Methane Hydrates Task of the APRISES initiative align closely with the priorities of P.L. 106-193, but emphasize those areas of particular relevance to the ONR and which are consistent with the overall goals of APRISES. Specifically, the development of hydrates and related sources of seafloor methane as logistical fuels for Naval applications, and related marine environmental issues, have been the principal areas of interest; exploratory drilling projects and seafloor stability/safety to date have received limited attention.
For APRICES16, the goals of the Methane Hydrates Task were to:

- Advance our understanding of the environmental impacts of natural seeps and accidental releases of methane and other hydrocarbons in the deep ocean;
- Explore the feasibility of sequestering CO$_2$ in natural methane hydrate reservoirs; and
- Promote international research collaborations on methane hydrates.

Technical accomplishments under the APRICES16 Methane Hydrates Task for each of these goals are described below.

**Environmental Impacts - Hydrate Formation on Natural Gas Bubbles**

When methane (CH$_4$) and other gaseous hydrocarbons are released accidentally into the ocean or from natural bottom seeps, they can lead to significant environmental consequences. These hydrocarbons can dissolve or may escape through the air-ocean interface. Microbial metabolism is recognized as a major sink of hydrocarbon contaminants in the ocean, but the mechanisms and rates of biological degradation and sedimentation are not well understood.

Methane is a potent greenhouse gas that has a global warming potential about 30 times larger than that of carbon dioxide (CO$_2$) [2]. The release of CH$_4$ during the aforementioned scenarios could increase its atmospheric inventory which may exacerbate climate change [3,4]. Investigations of the dissolution rate of buoyant natural gas bubbles rising through the oceanic water column are important in assessing environmental impacts since it will affect the resulting concentrations and spatial extent of the contamination zone. Bubbles that dissolve slowly relative to their vertical rise speed will distribute CH$_4$ and other natural gases over a wider area, resulting in lower concentrations. Furthermore, natural gas bubble plumes entrain ambient seawater as they rise through the density stratified deep ocean. During this ascent, volumes of cold, dense seawater drawn upward by a plume along with small gas bubbles dispersed in this water may detrain from the plume and form subsurface intrusion layers which are spread laterally by isopycnal transport [5]. Larger bubbles with strong buoyancy can resist this detrainment and continue to ascend toward the surface. Insight acquired from buoyant natural gas simulations is essential for environmental impact assessments.

To develop effective mitigation strategies for methane leakage in the deep ocean, investigations have been conducted to observe bubbles or plumes in the field and to measure bubble dissolution rates in the laboratory. Maini and Bishnoi [6] established a method to hold and observe rising bubbles in a fixed location for an extended period by utilizing a counter flow of water in a high-pressure vessel. They reported that a hydrate film formed on the rising CH$_4$ bubble. Masutani and Adams [7] used a large pressure vessel to observe pure CH$_4$ bubbles and oil covered CH$_4$ bubbles as part of a private-public risk assessment of deep offshore oil and gas production in the Gulf of Mexico. The dissolution process of CH$_4$ bubbles with and without hydrate films has also been
studied previously [8,9]. Warzinski et al. [10] and Chen et al. [11] performed detailed observations of the hydrate film formation on a CH$_4$ bubble to elucidate the dissolution process of the bubble. These investigations have revealed that, besides impeding dissolution, hydrate formation may also alter gas transport by changing the drag characteristics of the bubbles.

Several in situ experiments have examined rising bubbles and natural gas plumes. Topham [12] studied the behavior of natural gas bubbles released into the water column at depths of 650 and 325 m in the Beaufort Sea. Rehder et al. [13-15] released CH$_4$ and argon or CO$_2$ at the ocean floor in Monterey Bay and observed rising bubble behavior with a remotely operated vehicle (ROV). As part of the DeepSpill project, a field test was conducted to simulate a deep undersea well blowout in which significant quantities of oil and gas were discharged at a depth of 844 m at the Helland Hansen site in the Norwegian Sea, and the behavior of these plumes was studied [16]. Furthermore, natural gas bubbles released from the seabed were observed via acoustic sounder imaging at the Sakhalin slope in the Sea of Okhotsk [17], at the mud volcano in the Black Sea [18], and at Blake Ridge [19]. Recently, detailed observations of rising bubbles were performed via tracking with an ROV in the Gulf of Mexico [20,21].

Applying results of these earlier studies, models have been developed to simulate dissolution and dispersion of CH$_4$ bubbles rising through the oceanic water column. Johansen [22] proposed the Lagrangian DEEPBLOW model to assess oil and gas blowout accidents. Incorporating the results of laboratory and field experiments, Yapa and his colleagues modified Johansen’s model [23-25], and developed the Clarkson Deepwater Oil and Gas (CDOG) model to predict dissolution and transport of oil and gases in seawater [26,27]. McGinnis et al. [28] also proposed a model to simulate the behavior of CH$_4$ gas rising from the seafloor to the ocean surface.

Recently, as part of offshore CH$_4$-hydrate research and development activities, the Methane Gases from Deepwater (MEGADEEP) model [29] and MEGADEEP-Eco model [30] were created to simulate the diffusion behavior of CH$_4$ gas released from the seabed. These models were applied to CH$_4$-hydrate activities in the Nankai trough [31] by the MH21 project in Japan. They were also used to simulate CH$_4$ emission from offshore CH$_4$-hydrate reservoirs in the East China Sea [32] and in the Japan Sea [33].

Previous research has provided significant insight into the dissolution process of CH$_4$ bubbles in seawater; however, the majority of laboratory experiments have been performed using pure water and field studies have been conducted in seawater. The effect of salts on the dissolution rate of CH$_4$ bubbles is estimated only indirectly, and studies that made direct comparisons are limited. Furthermore, laboratory experiments mainly focused on the effects of the hydrate film formation on the dissolving bubbles, and only a very small number of measurements have been made of the bubble dissolution rate under non-hydrate forming conditions. In consideration of these deficiencies, we developed a facility and methods to measure the dissolution rate of CH$_4$ bubbles.
outside of the hydrate film forming regime. A description of the facility and a sample of preliminary data on the dissolution rate of single CH₄ bubbles are provided below.

**Materials and Methods:** Experiments were performed in a facility that can simulate conditions in the ocean from the surface down to 1000 m depth. The HNEI Deep Ocean Simulator (DOS) facility allows continuous monitoring of buoyant gas bubbles for extended periods. A downward flow of water over the rising bubble generates a downward drag force. The flow rate of water over the bubble can be adjusted so that buoyancy and drag forces are balanced and the bubble is held stationary in space. In the frame of reference of the bubble, this simulates buoyant rise through the water column. In this study, dissolution rates of single CH₄ bubbles under dynamic (i.e., advective), non-hydrate-forming conditions were inferred from data on bubble shrinkage over time.

The DOS has an internal volume of about 100 L and can operate safely at internal hydrostatic pressures up to 10.4 MPa. The DOS consists of a pressure vessel equipped with observation windows, a high-pressure water circulation system, a temperature controller, a gas supply system, and an imaging system. Previous studies [6,7] have confirmed that this system is capable of monitoring the behavior of single and multiple buoyant droplets and bubbles over long time periods.

![Deep Ocean Simulating (DOS) facility](image_url)

Figure 4.1. Schematic diagram of the Deep Ocean Simulator (DOS) facility.

Figure 4.1 presents a schematic diagram of the DOS facility. The cylindrical pressure chamber comprises two sections, each approximately 1 m in height. The upper section (146 mm inner
diameter) serves as a low-velocity, run-in plenum that supplies the enclosed water tunnel. The plastic water tunnel shown in the inset is mounted inside the 298 mm inner diameter lower section that is equipped with a pair of high-pressure viewports (J.M. Canty Fuseview Sightglass; approximately 100 mm clear aperture; 10.44 MPa maximum operating pressure) positioned opposite one another to allow observation of the bubbles in the water tunnel. Both sections are fabricated from 316 stainless steel in compliance with all applicable ASME pressure vessel codes. Inner surfaces of the chamber are coated with PTFE.

The system is filled with about 100 L of either tap water or synthetic seawater. While natural seawater was available for the present experiments, complications associated with variability of its properties were encountered in earlier investigations. To minimize this problem, and to ensure that results could be replicated by others, we elected to use artificial seawater with known composition and minimal biological loading.

Synthetic seawater is prepared by mixing Instant Ocean with tap water to obtain a salinity of 3.5 ± 0.2 wt.% NaCl. The Instant Ocean aquarium mix contains naturally occurring salts including sodium chloride, magnesium chloride, sodium sulfate, calcium chloride, and potassium chloride [34]. The pressurized liquid in the system is circulated with a variable speed, magnetically coupled gear pump (Micropump model 223/56 C; Leeson Micro Series AC Inverter, maximum discharge rate: 12 L/min). Two bath chillers (Thermo Scientific model ThermoChill III and model IsoTemp 6200) are employed to maintain water temperature in the range extending from 278 to 308 K, with an accuracy of ± 1 K. Water flow rate in the water tunnel can be adjusted between 5 and 50 cm/s. For a dissolving CH$_4$ bubble with a diameter between 10 and 1 mm, the flow rate in the water tunnel test section was adjusted over a range of approximately 20 to 16 cm/s.

The water tunnel consists of a clear acrylic inlet contraction and constant area viewing section cemented to a polycarbonate diffuser. The diffuser downstream of the viewing section ensures that gas bubbles under observation are not swept out of the water tunnel as they dissolve, since the downward fluid velocity decreases rapidly by a factor of about 20 from inlet to exit in the diffuser. This allows us periodically to adjust (i.e., reduce) the fluid flow rate and reposition the dissolving bubbles back in the viewing section for continued observation. The inlet contraction of the plastic water tunnel is employed to minimize boundary layers and reduce turbulence levels in the 25.4 mm inner diameter x 102 mm length, cylindrical test (viewing) section.

CH$_4$ gas prepared by Airgas, Inc. that was used in the experiments had 99.99% purity. The gas was injected into the water from a needle positioned at the base of the pressure vessel.

The clear, constant area viewing section of the water tunnel was aligned horizontally with the two large viewports. Gas bubbles stabilized with the downward flow of water were illuminated with an LED panel (Metaphase Technologies model FR-BL) mounted in front of one viewport and were monitored with a telecentric CCD camera (Prosilica GT1920 with Thorlabs 0.128 Bi-telecentric
lens) through the opposite viewport. The telecentric camera lens provided constant magnification across the span of the 25.4 mm inner diameter viewing section, to avoid errors in estimating changes in size over time of the dissolving bubbles as they wandered laterally toward and away from the camera.

Images were recorded at intervals of up to 0.5 s. Images were analyzed every 3 to 30 s depending on the size change rate. Image analysis was done post-experiment with LabView’s Vision software. Due to minor bubble movement during image capture, the spatial resolution of the image measurements was estimated to be 0.05 mm.

The shape of the bubble was assumed to be an oblate spheroid, and the major axis \((a)\) and the minor axis \((b)\) were estimated from the 2D image data. The time change of the spherical diameter \((d_e)\) of the equivalent volume \((v)\), calculated by Equation 4.1, was investigated.

\[
v = \pi (a^2b)/6 = \pi d_e^3/6
\]

(Equation 4.1)

The Heywood circularity factor \((H)\) also was calculated to assess the bubble-shape change. \(H\) is determined by dividing the observed perimeter of the bubble by the circumference of a circle with the same projected area. Deviations from circularity result in values of \(H >1\). Three or more replicates typically are performed at each test condition.

**Results:** Bubble dissolution data in the DOS collected over a range of operating temperatures in both tap water and sea water have been published in the open access journal *Energies* [35]. A brief summary of the results reported in that paper is provided below.

Figure 4.2 shows a typical image of a CH\(_4\) bubble observed in the high-pressure vessel. The buoyant bubble is stabilized with a downward flow of water.
Figures 4.3 and 4.4 show, respectively, bubble shrinkage (i.e., change in spherical diameter, $d_e$, with time) and the effect of temperature on the rate of shrinkage, $V = \frac{dd_e}{dt}$. Figure 4.4 also compares $V$ in tap water and sea water.
The present results indicate that CH$_4$ bubbles dissolve in pure water at approximately twice the rate of bubbles in seawater, and that dissolution rates in seawater appeared to increase slightly with temperature between 288 K and 303 K. These data were compared with corresponding dissolution rates calculated by models used in various seafloor gas hydrate development projects. The measured and predicted rates in pure water were in good agreement; however, experimental data obtained with seawater yielded smaller bubble shrinkage rates than the model results. The temperature dependency of the bubble dissolution rate observed in the experiments appear to suggest that the rate of dissolution of CH$_4$ bubbles is limited not by the rate of transfer of CH$_4$ molecules across the phase interface, but rather by the diffusion of dissolved CH$_4$ molecules from the interfacial zone to the bulk water phase. We propose that this rate-determining step be considered for inclusion in CH$_4$ bubble dissolution models to improve the accuracy of the model results.

**Sequestration - CO$_2$-CH$_4$ Hydrate Exchange**

Injection of CO$_2$ into methane hydrate reservoirs in sediment has been proposed as a means to destabilize the hydrate to release methane gas for energy, and to sequester CO$_2$ from the atmosphere. A number of laboratory experiments suggest that the exchange proceeds too slowly to be viable at a commercial-scale. Recently, however, new theoretical thermodynamic analyses have indicated that gas mixtures of N$_2$ and CO$_2$ may improve the kinetics of replacement of CH$_4$ with CO$_2$ in hydrate deposits [36]. In order to assess the feasibility of CO$_2$-CH$_4$ hydrate exchange for simultaneous methane production and carbon sequestration, experiments were performed employing our Setaram BT2.15 calorimeter to explore the energetics and kinetics of this process.
Materials and Methods: During these experiments, methane hydrate is formed in the sample cell of a Setaram BT2.15 calorimeter. Figure 4.5 presents a schematic diagram of the CO₂-CH₄ hydrate exchange facility. The calorimeter first is purged of atmospheric air using a vacuum pump and dry nitrogen gas. After purging, it is cooled to -10°C using liquid N₂. Following the protocol for methane hydrate synthesis developed previously and described in earlier HNEI reports, distilled deionized water is sprayed into a liquid N₂ bath to generate fine ice crystals. Crystals smaller than about 200 μm are collected, weighed, and loaded into a sample cell. The assembled cell is then inserted into the cold calorimeter test well, purged with N₂, and pressurized slowly with pure (99.99%) CH₄ gas prepared by Airgas, Inc.

When the pressure in the cell reached 7.0 MPa (1000 psig), the temperature of the calorimeter was increased from -10°C to -5°C and allowed to equilibrate. Once the calorimeter reached steady-state, the sample temperature was cycled between -5°C and 4°C over 12 hours. The calorimeter then was cooled to -10°C. This forced any remaining liquid water, which did not form hydrate, to freeze back to ice. After allowing the sample to reach equilibrium, it was then brought back up to 3°C before CO₂ injection.

For the CO₂ injection process, the sample cell was depressurized to 0.1 MPa (ambient pressure) and CO₂ gas at room temperature (~25°C) was quickly injected back into the cell until the pressure
reached 7.0 MPa. The sample was then held at 7.0 MPa and 3°C for 12 hours to allow the methane-to-CO₂ hydrate exchange to occur.

The CH₄ hydrate next was dissociated by slowly increasing temperature of the sample from 3°C to 6°C and holding the sample at 6°C. The corresponding thermograms exhibited an endothermic signature characteristic of dissociation. Finally, temperature was slowly increased from 5°C to 10°C to melt any CO₂ hydrate that had formed.

**Results:** The methane and CO₂ hydrate dissociation peaks, while observationally separate, was not easy to separate heat flows associated with each phenomenon. Therefore, a different method is suggested to obtain results for CO₂ and CH₄ hydrate exchange analyses. Further, the heat flows of methane hydrate dissociation were very irregular compared to previously performed methane dissociation experiments – possibly as a result of CO₂ hydrates forming concurrently with CH₄ hydrate dissociation. It also appears that CO₂ hydrates did not form in large quantities, as the heat flow corresponding to CO₂ hydrate dissociation is very small relative to the methane hydrate heat flow trough.

![Figure 4.6 Overview of experiment process: Methane Hydrate synthesis cycling, methane depressurization, CO₂ injection, CO₂ hydrate formation, and methane and CO₂ hydrate decomposition.](image)
Figure 4.7 Methane and CO$_2$ Hydrate dissociation heat flow. The small dip at roughly hour 27 and ~12°C is estimated to be CO$_2$ hydrate dissociation, the dip in the 23 hour mark is estimated to be methane hydrate dissociation. (Note: Figure 1 and 2 are of the same experiment, however due to how the processing program outputs combined data, the time scale is shifted.)

**International Collaborative Research and Development**

Pursuant to the goal of promoting international R&D cooperation on methane hydrates, that was a cornerstone of the methane hydrate task of the previous HEET program proposal, HNEI provided financial support and was a member of the Organizing Committee of the 11th International Fiery Ice Workshop on methane hydrates. Fiery Ice 2017 The 11th International Workshop on Methane Hydrate Research and Development was held in Corpus Christi, Texas on December 6th through 8th 2017. The 2.5-day workshop included five national reports, six breakout sessions, and 17 oral research presentations. Two poster sessions were also included in the agenda.

The national reports described the present status of gas hydrate research in the United States, China, Korea, and Japan. The breakout sessions were organized around six topics: 1) Laboratory experimentation; 2) Gas hydrate modeling; 3) Gas hydrate deep drilling; 4) Carbon sequestration related to gas hydrate mining; 5) Site assessment; and 6) Biogeochemical assessments of gas hydrate loading and monitoring environmental health.

Additional information on the workshop, including abstracts and presentation slides, are available in the workshop report. This report is available on the HNEI website.
Publications and Presentations

Peer-Reviewed Publications


References


**TASK 5: SECURE MICROGRIDS**

Under Task 5 Secure Microgrids, a range of projects were executed to develop, test, and integrate secure microgrid technology including distributed energy resources. The research efforts included the development and performance assessment of innovative technologies and methodologies aimed to improve or ensure the operability and resiliency of the electricity grid during natural disasters and intentional acts of disruption, as well as renewable energy generation and active management and control of the energy systems. The work described in the following sections was conducted primarily by HNEI’s GridSTART (Grid System Technologies Advanced Research Team).

### 5.1 Moloka‘i Dynamic Load Bank

The island of Moloka‘i is one of the smaller Hawaiian Islands in the central Pacific Ocean. Its isolated power system has a peak demand of 5.7 MW, a minimum evening demand of 2.2 MW, and serves a rural population of approximately 7,300 residents. At the start of 2019, the island had approximately 2.3 MW of distributed solar photovoltaic (PV) generation installed and approved for installation, which is predominantly behind-the-meter rooftop systems, and a 100kW grid-tied hydro project.

Among the challenges faced by utilities to integrate very high levels of rooftop solar PV on isolated island grids is maintaining a minimum reliable operating level of diesel generators during times of high PV production. High PV production can force generators below their required minimum operating point, with the uncontrolled “excess energy” produced by the PV systems degrading grid reliability and operating risk to unacceptable levels.
In March 2015, Maui Electric Company, Ltd. (MECO) informed customers that the Molokaʻi grid had reached its system-level PV hosting capacity limit. Since that time, customer applications for an additional 665 kW of distributed PV systems were held in a queue pending interconnection approval by the utility. In total, there was in excess of 3 MW of distributed generation installed, approved, or in the queue on the Molokaʻi system, which has a minimum daytime gross load of only 3.7 MW. The system-level PV hosting constraint is a function of the daytime load on the island, the uncontrolled power production from the existing and proposed new grid-tied PV systems in the queue, and the minimum reliable operating level of the must-run diesel generation on the island. The diesel generation on the island has a minimum reliable operating point of 1.3 MW; therefore, with a minimum daytime load of 3.7 MW, the utility determined that there is only room to accommodate a maximum of 2.4 MW of uncontrolled PV capacity on the system. Further, the high penetration of PV on the grid can exacerbate system stability challenges during foreseeable contingency events, such as a sudden loss of a generating unit or a power line fault, causing the system frequency to drop below 57 Hz within a few cycles. These sudden drops in frequency in turn cause distributed PV systems to trip offline, and this cascade effect can lead to an increase in load shedding or a system-wide blackout.

This project, a joint HNEI and MECO initiative, deployed a custom controlled Dynamic Load Bank (DLB) to deliver a practical, reliable, and inexpensive means to prevent the baseload diesel generators from operating below their minimum dispatch level, while enabling the grid connection of significantly more rooftop PV on Molokaʻi island. Project lessons will support enabling high penetration of distributed PV systems on microgrids and island power systems.

Specifically, this project analyzes the performance and effectiveness of a DLB as an “energy safety valve” to provide a near-term solution for increased solar interconnections and longer-term grid management asset for small island grid and microgrid applications. In this application, the DLB rapidly adds load to the Molokaʻi system using secure communications within the power plant when needed to balance the grid during infrequent periods of excess solar energy production. HNEI GridSTART’s analysis in Figure 5.1.1 illustrates that the potential for excess energy production by proposed rooftop PV systems held in the queue would occur very infrequently. By absorbing a mere 3.9 MWh of excess solar energy with the DLB, annual production of a significant 1.1 GWh of clean solar energy is enabled (with a commensurate reduction in fossil energy use) through the interconnection of all 665 kW of distributed PV in the queue. In contrast, investment in a battery energy storage system to capture the 3.9 MWh of excess solar energy production annually is not economically justified.
Under APRISES14, control algorithms for the primary use case of excess energy management were tested and verified. In November 2018, upon the load bank commissioning and implementation of these automated controls, the utility was able to add an additional 725 kW of distributed PV capacity to the system (even more than the 665 kW earlier held in queue by the utility). Extended research in DLB controls development were proposed and planned to potentially deliver additional grid value from this asset, such as fast frequency response to system dynamic events.

Under APRISES15, HNEI and MECO conducted field tests to determine if the DLB is capable of meeting the demands of fast frequency response. The tests included: (1) measuring the accuracy of the frequency readings from the DLB; and (2) measuring the latency between the Real-Time Automated Controller (RTAC) and the DLB. If the DLB was able to accurately read the grid frequency, it would eliminate the need for an external sensor. If the DLB could be controlled with a minimal time delay from the RTAC, it could be used for fast frequency response and lessen the severity of load shedding and over frequency events.

A PQube power meter with GPS time synchronization was installed at the DLB as a reference meter to verify the DLB readings. Data recorded simultaneously from the DLB and the PQube were compared to verify the accuracy of the DLB frequency readings and to measure the communication latency between the RTAC and the DLB. The RTAC was physically installed close to the DLB to minimize communication latency (Figure 5.1.2). The RTAC and DLB communicate over Ethernet cables using Modbus TCP/IP (Figure 5.1.3).
Figure 5.1.2. New control box containing the RTAC and reference PQube meter physically located near the DLB.

Figure 5.1.3. Block diagram of the DLB latency test.

Figure 5.1.4 shows relative frequency error measured by the DLB compared with the reference PQube power meter. As seen in the figure, the frequency measurements from the DLB are read every 200 ms (5 Hz) and can vary about ± 0.1 Hz from the reference. The PQube power meter used as a reference has an accuracy of ± 0.01% with a resolution of 0.0001 Hz, while the DLB has an accuracy of only ± 0.2% with a resolution of 0.01 Hz.
The latency test results shown in Figure 5.1.5 demonstrate that there is a mean latency of approximately 450 ms from the time when the RTAC sends a load change command to the time when the contactors in the DLB switch and change the load. Of the 450 ms of mean latency, a maximum of 100 ms of “built-in delay” comes from the time the DLB’s Sigma Controller receives the command to the time the contactors change (see Figure 5.1.3). This means the theoretical lowest total latency for the system is about 100 ms.

As Figure 5.1.6 shows, a possible solution to minimize latency is to use Modbus RTU directly from the RTAC to the DLB. Protocol overhead and translation steps used in Modbus TCP/IP may be adding significant delays in the communication between the RTAC and the DLB.
Figure 5.1.6. Proposed block diagram for minimizing latency by using Modbus RTU directly from the RTAC to the DLB.

Under APRISES16, this information was presented to MECO and following careful consideration, it was determined that available engineering resources were inadequate to meet the substantial time and effort required to coordinate and tune the controls of the DLB with the existing fast-frequency responsive BESS on island. While the capabilities of the DLB appear able to contribute incremental support in mitigating impact severity of under-frequency events (e.g., avoid shedding a “kicker” load block in the Molokaʻi automatic under-frequency load shedding scheme), the existing BESS was delivering adequate grid-stabilizing dynamic response for effective system operation. Thus, in this context, the demand placed upon the scarce engineering resources available on the small Molokaʻi island utility outweighed the incremental fast frequency response benefit the DLB offered. HNEI greatly values its successful partnership with MECO in co-developing and delivering practical and cost-effective solutions that have significantly increased renewable energy uptake and offered Molokaʻi residents a cleaner energy future.

5.2 Bidirectional EV Charging Optimization

Although the shift towards electric vehicles (EVs) can pose new challenges to the electric grid system with increased electricity demand and reshaped grid loads, an immense opportunity exists to leverage the potential flexibility of EVs to provide user benefits and grid services through managed charging. These benefits and services can deliver economic value to EV owners while potentially enhancing the grid’s reliability and resiliency. However, the optimization problem is complex due to the numerous categories and variants of grid services along with factors, such as potential degradation impact on EV batteries, vehicle owner preferences, and scheduling
requirements. To tackle the complex optimization problem and demonstrate the use of bidirectional EV chargers, HNEI GridSTART is developing and evaluating the performance of novel algorithms that optimize the charge/discharge schedules of shared fleet EVs under this demonstration project.

The novel EV charger control algorithms will first ensure that the shared vehicles for the designated University of Hawai‘i (UH) use are efficiently assigned and readily available for transport needs. Simultaneously, the controls could deliver ancillary power and energy services through intelligent EV charge and discharge commands, at times allowing the stored energy in the EV batteries to be strategically withdrawn to minimize the overall cost of energy supply to UH campus loads and possibly support the operational needs of the local utility operator (i.e., Hawaiian Electric Company) through the supply of grid ancillary services in return for financial compensation. The algorithms also incorporate data fed from state-of-the-art in-house developed forecasts of campus building demand and on-campus solar PV power production, thus maximizing the use of renewable energy as the preferred source for EV charging and supply to building loads, while minimizing costly energy purchases from the grid.

The experiences and results of the current project will inform UH at Mānoa (UHM) consideration of options, such as the electrification of fleet vehicles, advanced car share applications, integration of distributed renewable energy resources on campus, and the optimal management of campus energy use and cost containment by virtue of the stored energy in the vehicle batteries. Additionally, this project’s field test results can be scaled to evaluate a larger fleet of EVs under a car-sharing system acting in aggregate to support grid ancillary services.

HNEI is collaborating with IKS Co., Ltd. on technology development, testing, and demonstration of advanced control of two bidirectional EV chargers (H-PCS) installed on the UHM campus. The H-PCS device was developed by IKS with support from Hitachi Limited as part of the earlier JUMPSmart Maui smart grid demonstration project, in which HNEI was a project partner. Figure 5.2.1 shows the two 6 kVA H-PCS, provided on loan by IKS for the duration of the two-year demonstration project, and the rest of the project’s hardware including two 7.5 kVA single-phase three-wire 208Y-120/240V transformers and a control box. A new 3 phase 208Y/120V distribution panel was also installed at the demonstration site.
Two EVs procured by the project for this research will be accessed via an HNEI GridSTART developed secure smartphone/web-based car scheduling application made available to the drivers. Not only will the EVs be used for energy research and results in dissemination, but the project experience will also allow the UH administration to evaluate the practical use of EVs as part of their vehicle fleet. Figure 5.2.2 shows a functional system diagram for the above described components.
A detailed description of the functional system diagram follows:

1) **Load Forecast**: A meter/controller developed by HNEI Grid will be used to measure the load at the charging location. Measured and historical data for the location will be used by a machine learning (ML) algorithm to forecast the gross demand over a range of horizons from hours to a day ahead. The forecasted load profile will be fed into the optimized charging (OC) algorithm.

2) **PV Forecast**: HNEI Grid has developed a multi-scale solar forecasting system under previous APRISES funding. It can monitor irradiance in near real-time and generate PV power forecasts from minutes to days ahead based on a long-term observation database and the analysis of satellite data. This system is fully automated, generating predictions without human intervention. This solar power forecasting technique will be used to stream PV system production forecasts at the charging location. The data will be supplied to the OC algorithm on the controller as a PV forecast input.

3) **Power Monitoring Devices**: The devices will measure the building’s load and power output of PV panels. The measured data will be used to create a load forecast for upcoming hours. The PV system’s power output will be measured to judge the accuracy of the PV forecast. All measured data will be saved in the Grid server to be used for system performance analysis.
4) Controller/Meter (ARGEMS): Under previous APRISES funding, HNEI developed the Advanced Real-Time Grid Energy Monitor System (ARGEMS). It offers high-fidelity voltage and current measurements, numerous communications options, low-latency event-driven messaging, precise GPS-based timing, backup power supply, and powerful processing for real-time data analysis—all in a small weather-resistant enclosure. ARGEMS will be used on-site within the control box to stream the data/commands from an HNEI server to the EV chargers and vice versa.

5) Reservation Request (EV Scheduling Information): HNEI GridSTART is developing web-based software that will help EV drivers reserve the cars for use. The software is designed, coded, and integrated to optimize charge/discharge schedules for the EVs. Scheduling information will come from the software through a server. The scalable design of this software will enable its application to a larger a larger EV fleet in the future.

6) GridSTART Server: All measurements will be kept on a GridSTART server. Based on the measured and historical data, the OC and scheduling algorithms will run on the server, and commands will be sent to the EV chargers for execution.

7) H-PCS1 and H-PCS2: Two bidirectional EV chargers (H-PCS1 and H-PCS2) are presently being commissioned by HNEI and IKS engineers. Under a Standard Interconnection Agreement with the Hawaiian Electric Company, both H-PCS are approved to operate in parallel with the utility grid as the first bidirectional EV chargers in use on O‘ahu. With the ability of these bidirectional EV chargers to utilize solar PV power as a direct source of energy for EV charging, the OC algorithm will incorporate HNEI’s solar forecasting to maximize solar power as the preferred source of energy while minimizing EV charging costs.

Major project activities completed under APRISES16 include:

- Finalizing electrical installation drawings;
- Developing a bid package for the final construction and field installation work for the EV chargers’ installation and all associated electrical ties;
- Awarding the construction contract to a contractor;
- Working with the contractor to install the EV chargers, control box, transformers, and required electrical panels;
- Finalizing the web scheduling software; and
- Continuing the development and improvement of the overall architecture of the proposed OC algorithm.

Under future APRISES funding, the web-based car reservation software will be finalized. This reservation software will be fully integrated with the novel customized software to optimize charge/discharge schedules for the EVs. This will enable HNEI GridSTART to transition into the testing and evaluation phases of the research.
5.3 Hawai‘i Virtual Power Plant Demonstration

The objective of this project is to analyze the tradeoffs and demonstrate the economic dispatch of numerous customer- and utility-side energy/power services from multiple combined behind-the-meter (BTM) battery energy storage system plus photovoltaic (BESS + PV) units. Each BESS + PV unit is small—designed to support a single family residence (several kilowatts, kW)—but at large numbers these units could produce power that is comparable to traditional power plants (typically tens or even hundreds of megawatts, MW). At this scale, the system of systems is called a virtual power plant (VPP) because it relies on communications and software to collectively adjust the power production of physical assets that may already exist—in this case residential-scale BESS + PV units. This project is expected to provide important insights into the functional/economic trade-offs in VPP dispatch of BESS + PV resources that can help outline and quantify the business case for VPPs, including the value proposition for customer participation in a VPP and utility utilization of the same.

In this project, HNEI Grid START is utilizing four Sunverge Solar Integration System (SIS) distributed BESS + PV units (each with a 5 kW/12.3 kWh battery and 2.5 kW PV) which were acquired at no direct cost from the New and Industrial Technology Development Organization (NEDO) of Japan. These were previously installed at the business office of Haleakalā Solar (220 Lalo St, Kahului, HI) under the NEDO funded JUMPSmart Maui (JSM) smart grid project.

Under APRISES14, a new electrical service was installed to connect the SIS BESS units at the Haleakalā Solar location to the MECO power system and loads at the location were also transferred to the new service. All required county permits were obtained, after a few significant delays, and a conditional approval for the connection of the SIS BESS systems was obtained from MECO. Also, progress was made on defining the valuation methods and data needs, telemetry, collection, and warehousing for data required to assess the customer and utility use cases.

Under APRISES15, final site and equipment inspection was completed by MECO. It was found that battery remediation work was required to bring the SIS units into operation, and this was completed. The units were connected to the Sunverge Software Platform (SSP), which has a web front end for establishing various rulesets and sequences for SIS operation. The units were operated with a baseline ruleset where 500 W of PV power was used to charge the batteries during the day until 95% state of charge (SOC). All excess PV power was exported to the grid. In the evening, the batteries were discharged at 500 W down to 50% SOC. Figure 5.3.1 shows the SSP’s main dashboard, where four units were online and operating according to the baseline ruleset shown in Figure 5.3.2.
Figure 5.3.1. Dashboard of the Sunverge Software Platform (SSP).

Figure 5.3.2. SSP viewer/editor for the baseline ruleset.
Ultimately, it was determined that the SSP rulesets were too limited to allow the full, dynamic economic optimization desired for the project. In addition, Sunverge was not able to provide sufficient documentation about how the system interprets and follows some aspects of the rules and how they are layered or combined. For this reason, under APRIZES16, HNEI Grid\textit{START} designed and implemented a web-based method to utilize the existing SSP website to allow external optimization algorithms and software to monitor and control the SIS units. This was challenging and labor-intensive because the website is designed for human interaction, not as an application programming interface (API). HNEI Grid\textit{START} also formally defined the optimization problem, which includes services for capacity build, capacity reduction, and backup power.

After evaluating several candidate optimization solvers, HNEI Grid\textit{START} began to implement and evaluate the solution to the optimization problem in Gurobi (Gurobi Optimization LLC, Beaverton, OR). Synergies between this project and the bidirectional EV charging project were identified and leveraged. For example, the following questions were discussed and addressed for both projects:

1) How to properly account for difference between starting and ending state of charge of a battery over the planning horizon; and
2) How to reduce or eliminate the potential oscillation between charge and discharge states.

HNEI has contracted Haleakalā Solar to install a metering box using HNEI’s Advanced Realtime Grid Energy Monitor System (ARGEMS). The challenge in preparing the system was how to provide ongoing configuration and maintenance of the system while it is installed on a private Local Area Network (LAN). The box (Figure 5.3.3) will independently monitor the power consumption of four heating, ventilation, and air conditioning (HVAC) systems, each comprised of a condenser and an air handler, plus the main supply to the HVAC panel. In a typical test scenario, HNEI plans to economically dispatch the four BESS + PV units according to the defined optimization problem and the time-varying load profiles of the four HVAC systems in conjunction with PV generation.
Future work includes evaluating the optimization framework on the four BESS + PV units at Haleakalā Solar. HNEI Grid\textit{START} plans to perform a sensitivity study by sweeping parameters such as the value of backup power and the economic parameters affecting customer reimbursement for grid services. HNEI Grid\textit{START} also plans to explore and parameterize where possible the demand and supply curves of various grid services from the combined BESS + PV units as a VPP. Associated research questions include:

1) Which customer and grid services are most synergistic; i.e., which customer and grid services offer the best combined value proposition?
2) To what extent is a heuristic- or prioritization-based approach appropriate for layering or stacking services? What additional economic benefit will a full optimization provide?; and
3) What are the supply curves for VPP-based grid services from BESS + PV (while competing with customer services) under various available or proposed utility programs?

5.4 Coconut Island DC Microgrid

Coconut Island (Moku O Loʻe) is a 28-acre (113,000 m²) island in Kāneʻohe Bay off the island of Oʻahu and is home to the Hawaiʻi Institute of Marine Biology (HIMB) of the University of Hawaiʻi. One of HIMB’s goals is to make the island and its research facilities a model for sustainable systems. As such, it is an ideal site for a renewable energy technology-based test bed,
particularly representative of an isolated location vulnerable to energy disruption yet serving critical power needs essential to the research and educational mission of HIMB. This island is an inherent microgrid served via an undersea electrical connection tied to a single distribution circuit owned and operated by the local utility on O‘ahu. The tropical marine features of the island further its attractiveness as a unique microgrid test bed. Its exposure to persistent on-shore winds and highly corrosive salt spray allows for material and technology testing in a micro-climate representative of those potentially encountered in coastal installations of Navy’s interest.

The Coconut Island DC Microgrid Project was initiated under previous APRISES funding with the project objective of demonstrating the performance and resilience of a DC microgrid designed to serve loads within two buildings on Coconut Island, including reliable power to critical loads during interruptions of grid supplied power, and providing the island with clean electrified transportation options powered primarily by the sun. The project has the following goals:

- Demonstrate innovative new clean energy technologies;
- Reduce island energy dependence upon the local utility and the existing aged undersea electrical service tie, enhancing energy resilience for the selected critical loads;
- Provide a research platform to study DC microgrid resources and loads (e.g., energy storage and supporting technology and DC power appliances) in a tropical coastal environment;
- Increase island energy sustainability; and
- Provide solar electric powered land and sea based transportation options for HIMB.

The project integrates a DC distribution system into two existing buildings on the island, the Marine Mammal Research Project (MMRP) building and the adjacent Boat House, both depicted in Figure 5.4.1 below. The energy needs of the two buildings are currently served by AC power through one of the utility-owned electric service transformers located on island.
Major project activities completed through the support of prior APRlSES funding include:

- Project planning and permitting;
- Baseline energy use data metering and collection;
- Developing a conceptual design of the DC microgrid architecture to be integrated with the existing AC building infrastructure;
- Energy use and economic modeling to appropriately size a new rooftop PV system for installation on the MMRP building and a stationary battery energy storage system (BESS);
- In collaboration with the Okinawa Institute of Science and Technology and the PUES Corporation, Japan (“PUES”), specifying, designing, and procuring an electric E-car and E-boat as well as emergency power source powered by swappable BESS units charged via a swap battery charging station to be fed by the DC microgrid;
- Developing and installing two PV systems on the E-boat, one system to charge the swappable batteries on the boat and the other system to power auxiliary loads, such as an onboard radio;
- Testing and commissioning the E-Boat, including operational sea trials;
- Performing a due diligence assessment for potential partnering with Sion Electric Co., Ltd. (“Sion Electric”), a Japanese company with innovative DC microgrid controller technology that has been integrated with stationary BESS, DC powered lighting, and air conditioning loads in the course of prior technology development work in Japan. Unfortunately, the collaboration with Sion Electric did not prove to be a feasible option for this project;
- Initiating competitive procurement of the materials and installation services for the MMRP building 6.16 kW DC rooftop PV system to serve as the primary source of renewable energy for the DC microgrid;
• Commissioning the 6.16 kW rooftop PV system on the MMRP building;
• Procuring an 8 kW/8 kWh stationary battery;
• Procuring an AC/DC powered air conditioner and AC/DC LED lighting;
• Developing and procuring the DC microgrid controller and associated enclosures for the control system;
• Developing detailed electrical design drawings of the system; and
• Procuring contactors for engineering and electrical systems installation work.

As previously noted, HNEI Grid worked closely with PUES, a key collaborative research partner on this project, to adapt, improve upon, and install their swap battery charging station and associated E-car and E-boat. Figures 5.4.2 and Figure 5.4.3 show the installed battery charging station, portable swappable BESS units, and the commissioned E-Boat in sea trials. The 6.16 kW DC rooftop PV system on the MMRP building is shown in Figure 5.4.4.

Figure 5.4.2. Swap battery charging station and portable BESS units.

Figure 5.4.3. E-Boat in operation in Kāneʻohe Bay, Hawai‘i.
While exploring potential partnerships in Indonesia under the ONR funded Asia Pacific Regional Energy System Assessment (APRESA) award, HNEI met with the Director of the Tropical Renewable Energy Center (TREC) at the University of Indonesia. TREC has developed a prototype 2.5 kW DC-DC converter designed to serve DC loads from a 24 V bus and deployed it in a demonstration on the University of Indonesia campus. As this device had potential to fill a critical need for this project, a research collaboration was formed with TREC under APRINESS15 to develop and incorporate three (3) second generation “DCON” devices into the Coconut Island microgrid conceptual design as shown as item 5 in Figure 5.4.7.

Under APRINESS16 funding, the TREC team from the University of Indonesia manufactured, delivered and travelled to Hawai‘i to commission the three (3) second generation DCON devices for use in the Coconut Island DC microgrid.
Figure 5.4.5. Dr. Eko adhi Setiawan and TREC members at the HNEI office.

Figure 5.4.6. TREC team working with HNEI to install and commission the DCON devices.
Figure 5.4.7. DC microgrid electrical diagram with the numbered elements described below:

1) PV modules installed on the MMRP rooftop as the primary source of renewable energy for the microgrid. The PV system capacity was sized at 6.16 kW DC, which will generate enough energy to support the buildings’ targeted loads. PV panels were specified and designed to provide the necessary input DC voltage for effective integration with the DC microgrid controller;

2) Rectifier to manage the power provided to the DC bus from the grid;

3) Charge controller to manage power to the DC bus from the PV system;

4) An 8 kW/8 kWh stationary BESS used to store excess PV energy produced and export the excess energy to the DC microgrid when needed to minimize the use of utility supplied power during normal operation and to maintain service to the specified critical loads in the event of utility service disruption;

5) Three University of Indonesia TREC 2.5 kW “DCON” devices that manage voltage and current to power the DC loads of the microgrid from the 48V bus;

6) Inverter with a capacity appropriate to supply designated critical AC end-use loads within the MMRP building served by the DC microgrid (e.g., computers, Wi-Fi network, etc.);

7) An air conditioning unit that is able to operate with either a DC or AC power source. Its operating performance and efficiency under both DC and AC modes of operation will be assessed and compared;

8) A swap battery charging station, designed and manufactured by PUES, will charge the swappable BESS units used interchangeably in the E-boat, E-car and a portable power “suitcase battery” system. This station is capable of charging twelve (12) portable BESS units through the microgrid DC bus. The capacity of each BESS unit is rated at 1.4 kW and 1.4 kWh;

9) Interior LED lighting for the MMRP building that will be modified to allow operation with either a DC or AC power source;

10) AC and DC metering for performance data capture and analysis;

11) Microgrid controller that monitors and controls the operation of the microgrid; and

12) Contactor switches to control the mode of operation (AC or DC) of the microgrid.
With the major components procured under APRISES15, HNEI GridSTART applied APRISES16 funding to procure the balance of the microgrid system components and infrastructure installation, including the construction and build-out of a control room next to the MMRP building. HNEI GridSTART also installed the major components of the system within the control room, which are shown in Figures 5.4.8, 5.4.9, and 5.4.10.

Figure 5.4.8. Installed Blue Ion Stationary Battery System.

Figure 5.4.9. Microgrid Control System Contactors.
Under future APRISES funding, HNEI will complete the installation and commissioning of the DC microgrid system now that the purchase and installation of the major system components has been completed. This will enable HNEI GridSTART to move into the testing and evaluation phases of the research. HNEI GridSTART will monitor, characterize, and identify the performance, energy efficiency benefits, and limitations of DC operation in comparison to legacy AC supply of loads, and analyze the sustainability and resiliency benefits associated with the renewable energy powered DC microgrid operation and integrated electrified transportation alternatives.

**TASK 6: OCEAN ENERGY**

The Ocean Energy Task supported projects in two areas. Under subcontract to HNEI, Makai Ocean Engineering, located within the Natural Energy Lab of Hawai‘i Authority (NELHA) in Kailua-Kona, Hawai‘i, continued efforts to develop thin foil heat exchangers applicable to Ocean Thermal Energy Conversion as well as a variety of other U.S. Department of Defense (DOD) applications. In support of potential sea water air conditioning for Honolulu on the Island of O‘ahu, HNEI collaborated with the University of Hawai‘i’s Department of Oceanography to develop a thorough understanding of the baseline oceanographic conditions at the proposed site of the Honolulu SWAC system.
6.1 Ocean Thermal Energy Conversion (OTEC)

Makai Ocean Engineering has been developing Thin Foil Heat Exchangers (TFHX) for use in seawater-refrigerant, air-water, and water-water applications. In this period, Makai’s efforts focused on advancing the TFHX design, reducing TFHX fabrication time, and continuing to characterize TFHX thermal, hydraulic, and structural/mechanical performance. Between February 2020-July 2021, Makai made significant progress in advancing the TFHX design, reducing TFHX fabrication time/cost, and adding empirical data to TFHX thermal, hydraulic, and structural/mechanical performance database. In doing so, Makai continues to gain expertise in the fundamental principles of laser welding and further our understanding of the TFHX technology.

A brief summary of progress made during this period follows. Additional detail is provided in Makai Ocean Engineering’s final report to HNEI, which can be found at https://www.hnei.hawaii.edu/publications/project-reports/aprises-16/.

**TFHX Design**: A new, modular, 4-port, 1 m long, counterflow TFHX was designed for seawater-seawater and ammonia-seawater applications. This new plate design required a larger manifold opening and new forms and fixtures for fabrication. The modular design streamlines the assembly process for TFHX units but maintains TFHX customizability in internal/external channel sizes. Although some issues were identified during commissioning, Makai was still able to fabricate several full-length plates. In the next period, Makai’s efforts will include assembling and performance testing several modules in the 100 kW Test Station.

Makai also demonstrated the ability to perform the internal manifold weld for the all-welded version of a TFHX. The all-welded technology eliminates the need for gaskets (and accompanying inserts and hardware) to seal the internal fluid. After successful demonstration of the all-welded concept, Makai developed and demonstrated a new method to perform the internal manifold weld that is transferrable to different manifold sizes. Fixturing to perform the weld on stacks of multiple plates has been procured and Makai intends to test the sealing capability of a stack of all-welded plates next.

A new short-length plate (and accompanying fabrication fixtures) was designed for the all-welded platform. The short-length plate can be fabricated entirely in-house from coils of foil; there is no external vendor-performed forming step. The short-length plate also provides a rapid and economical platform for future TFHX characterization.

**TFHX Fabrication and Cost**: Makai commissioned the High Speed Welding Station (HSWS) and has already reduced fabrication times from 30 minutes to produce a mid-length 3E-style plate on the stage to 17.5 minutes to produce a full-length plate on the HSWS. TFHX cost has been reduced from $1297/m² for 3E-INT to $679/m² at current HSWS capacity and projected to decrease $608/m² in September after the arrival of new equipment for the HSWS. It is important to note
that previous costs did not include additional parts to build a TFHX unit, only the cost of plate fabrication; furthermore, current costs include more realistic contingency and operational expenses.

Issues with weld quality and reliability were identified during commissioning. Makai has resolved issues related to shield gas management with a plenum-type design and is confident modifications to laser and optical equipment will resolve remaining issues. Makai is currently awaiting delivery of additional optics.

A laser cutting method was developed to remove the excess foil from fabricated plates; plate quality and fabrication time improved over previous manual foil removal methods. A separate laser cutting system was purchased and will streamline TFHX fabrication. Makai is waiting for our new fabrication space to be completed to install the laser cutting system.

**TFHX Characterization and Performance:** In this period, Makai introduced additional weld parameters that expanded TFHX pressure capacity and channel sizes and began geometric and mechanical characterization of these new combinations. Makai developed a new plan for TFHX characterization that focuses on relevant TFHX design configurations, i.e., only testing plates fabricated with optimal weld parameters, expanded to required percentages, with appropriately designed seal welds and transition zones. In addition to using static and cyclic pressure testing to evaluate TFHX designs, Makai also added optical microscopy to the array of tools used in characterization.

Makai continues to conduct performance testing of different TFHX configurations. A new round of counterflow seawater-seawater performance testing was conducted at the 100 kW Test Station. Makai also completed modifications to the 100 kW testing station in preparation for full-length, modular, 4-port TFHX testing in counterflow seawater-seawater and seawater-ammonia configurations.

Makai also completed air-water performance testing of 11 TFHX configurations. The Air Convection Test Station was upgraded to accommodate higher flow rates and higher duties for more robust data collection. Previous trends of higher convective coefficients in smaller channels for the same Reynolds number and higher convective coefficients in larger channels for the same pressure drop were observed. More significantly, at tested air flow rates, the TFHX does not exhibit a saturation point – unlike finned heat exchangers, TFHX duty and performance continue to increase with increasing air flow rates.

Makai also performed a commercial case study for Trevi Systems, a company specializing in desalination projects. Makai designed and tested a TFHX at provided operating conditions and used the data to design TFHXs for a full-scale desalination system. Trevi Systems was impressed
with the technical performance and capabilities of the TFHX, but the current fabrication capacity and cost did not meet their project timeline or budget.

Work under future awards will be directed to resolve weld reliability/quality issues on the HSWS; fabricate 3-4 full-length modules for performance testing in ammonia-seawater and seawater-seawater orientations; and advance the all-welded TFHX technology by fabricating a stack of all-welded plates and performing a seal test to evaluate the internal manifold weld strength. Further development in automating the process is also planned; and utilize the short-length platform for TFHX characterization with existing titanium foil thicknesses and new materials, e.g., SS316L, Haynes 230.

6.2 SWAC Ocean Monitoring

Seawater air conditioning (SWAC) is a type of renewable energy that utilizes deep, cold seawater as a nearly carbon-neutral source of air conditioning coolant. The proposed Honolulu SWAC system was initially designed to draw deep, cold seawater from 500 m and release effluent via diffuser at 100-140 m. The objective of this project, in collaboration with the University of Hawai‘i’s Department of Oceanography, was to develop a thorough understanding of the baseline oceanographic conditions at the proposed site of the Honolulu SWAC system. At this time, the proposed SWAC plant for Honolulu will not be constructed as previously planned, however, the results of this monitoring effort can continue be utilized to: (1) assess the potential environmental impacts of a seawater air conditioning system on Māmala Bay or other potential developments and (2) provide insight into the nearshore oceanography of O‘ahu and how it differs from more oceanic locations nearby.

Sampling and data collection for this SWAC monitoring project was ended in December 2020 and included shipboard CTD profiling and bottom mooring deployments. This long term sampling effort resulted in high quality time series oceanographic data for parameters including currents, temperature, chlorophyll-a, dissolved inorganic carbon, nutrients, dissolved oxygen, methane, nitrous oxide, and phytoplankton. These parameters were measured at the proposed intake (500 m) and effluent (100-140 m) locations. The key results from the project include a better understanding of currents and of the depth and variability of the mixed layer within the bay and outside it.

Under previous APRISES awards, these efforts found that bathymetric forcing from a canyon, along with island-scale internal tides, increased the variability in temperature, nutrient, and oxygen variability in the near bottom environment of Māmala Bay [1]. A daily across-slope migration of the mesopelagic boundary community was also observed [2], since this community is an important part of the near-island food web by providing food for spinner dolphins and other predators. It
was discovered that they would interact with effluent waters of a SWAC plant in their nighttime shallower habitat.

Final sample analyses and the characterization of the onshore-offshore trends in phytoplankton are being completed, which will help to better understand the shifts in phytoplankton communities driven by the island mass effect (the increase in productivity near islands in oligotrophic systems). Another publication is being prepared and will be available on the HNEI website upon publication.

References


**TASK 7: ENERGY EFFICIENCY & TRANSPORTATION**

Task 7 comprises of two subtasks. Under Subtask 7.1, HNEI supported Ka Honua Momona (KHM) on Moloka‘i, Hawai‘i, a small off-grid compound with PV and wind generation, as a proof-of-concept site to demonstrate a control scheme to optimize battery use and reduce inverter losses; and a second project focused on implemented Light Detection and Ranging (LiDAR) based adaptive lighting systems to demonstrate the technology’s potential to reduce energy costs while improving security. Under Subtask 7.2, an analysis was conducted to assess the impact on fossil fuel use and emissions with the transition from internal combustion engine (ICE) to plug-in electric vehicles (EVs) on O‘ahu. Details of both subtasks follow.

**7.1 Energy Efficiency**

Two major projects were undertaken in Subtask 7.1. The first project focused on improving the efficacy of a small, off-grid renewable energy system using voltage sensing controls to manage energy supply and demand. Under the second project, a Light Detection and Ranging (LiDAR) based adaptive lighting systems was designed and installed at two sites, the University of Hawai‘i at Mānoa and Navy Facilities Engineering Command (NAVFAC) Hawai‘i facilities on O‘ahu, to demonstrate the potential to reduce energy costs while improving security.
Off-Grid Renewable Energy Nanogrid System

Ka Honua Momona (KHM), on Moloka‘i, Hawai‘i, is a not-for-profit organization that supports the local Hawaiian community on Moloka‘i by providing sustainable and cultural education that revitalize natural and cultural resources to perpetuate traditions, knowledge, and stewardship, while evolving with modern technologies. The compound includes several site loads: an office, a two restroom/shower building, two outdoor meeting facilities, a storage shed, and an aquaponics operation (Figure 7.1.1). The KHM compound is powered by a small 100% off-grid energy system comprising PV and wind generation with limited battery energy storage.

![Figure 7.1.1. Ka Honua Momona off-grid renewable energy nanogrid site in Kaunakakai, Moloka‘i.](image)

Under previous APRISES awards, KHM collaborated with HNEI to develop an online dashboard providing visualization of the energy use and renewable energy production of their off-grid energy system for community education purposes. Under this award, the KHM compound was used as a proof-of-concept site to demonstrate a control scheme to optimize battery use, reduce inverter losses, and utilize energy that is otherwise wasted when a battery system can no longer store additional energy due to capacity constraints.

A key factor of KHM’s operation is that its use is intermittent and therefore has variable daily loads that range from less than 300 W baseload on unoccupied days to a full 4,000 W load when sponsoring community events. During the unoccupied days, up to 18 kWh of excess renewable energy would be available for PV generation, but is not stored due to full batteries from previous day of non-use.
In 2019, nine Sunverge integrated energy modules (a Li-ion battery storage, inverter, charge controller, and communicator that sensed grid power) were donated to HNEI from the sponsors of a then-completed grid integration project in Maui. Because of its needs, KHM became a candidate for the Sunverge systems and three of these units were allocated to KHM to supplement their existing battery storage. By incorporating a dump load circuit and adding load and storage management controls, KHM was able to add power-based services (e.g. hot water and water distillation) and improve operations, while also improving the efficacy of their off-grid system.

With a finite area of rooftop for additional solar PV panels and limited physical space for battery storage, the goal of this effort was to improve system reliability and efficacy, reduce dependence on the fossil fuel backup generation, and provide additional qualitative services, by modifying how the energy is stored and dispatched. However, during the course of the project, it was found that in an off-utility-grid mode, the Sunverge inverter systems used significant amounts of energy in a non-loaded standby condition, depleting the batteries each night. This necessitated a mid-course correction dubbed “predictive look ahead programming,” a network of programmable auto transfer switches (ATS) and controls that reduced the system losses significantly by energizing the inverter only on an as-needed basis. This shift changed the dynamic of the project from that of load-side management to supply-side management, while maintaining the overall project objectives.

HNEI’s objectives for this project were to:

1) Develop a load shifting scheme to maximize utilization on a site whose load profiles have intermittent and varying loads and finite battery storage capacity;

2) Increase system utility by adding load dumps (“opportunity loads”) to utilize more available energy and simultaneously improve quality of life services (e.g., domestic hot water and water distillation); and

3) Test a “smart” predictive look ahead programming control strategy to match solar generation with partitioned battery storage in order to minimize inverter standby losses as the KHM losses were disproportionately large for a small 5.3 kW renewable grid.

Additionally, KHM’s goals were to: 1) reduce dependence on fossil fuel generation; 2) increase useful energy extracted from PV system and minimizing wasted generation; 3) minimize service interruptions; and 4) increase quality of life without sacrificing power delivery.

This project demonstrated that small off-grid renewable energy systems can significantly improve the utilization of the available energy sources (specifically, solar photovoltaic energy) by eliminating unnecessary inverter standby losses and adding opportunity loads to utilize excess available energy that may not otherwise be captured due to limited battery capacity.
Original Site Operational Profile

The initial KHM off-grid system was comprised of eighteen 240W PV panels (5.3 kW), two dual 3600-watt Outback inverters, one 80-amp Outback charge controller, and a dual string of sixteen 6-volt Rolls Surrette, flooded lead acid, deep cycle batteries for 40 kWh of total storage with 20 kWh useful storage, assuming a 50% depth of discharge (DoD).

A small baseload consisting of a refrigerator and office support loads (IT and communication servers and miscellaneous small loads) shaped one of several common daily profiles, while on other days, large on-site gatherings lasting well into the evening, exceeded battery capacity and required supplemental power from the fossil fuel-based standby generator. Figure 7.1.2 is an example 24-hour load profile that shows baseload typical operating conditions and a few short spikes of peak load. During a power loss, an electro-mechanical auto transfer switch triggered the auto-start stand-by generator with approximately a 5 second momentary outage. The generator transferred back to battery power when batteries were fully charged and non-essential loads such as air conditioning were shed when on generator power. No hot water existed on the site, in spite of kitchen and showering needs.

![Image of load profile]

Figure 7.1.2. 24-hour load profile with varying load conditions: baseload (250 W), typical (2,000 W) and short peaks (2,700-3,000 W).

The original project plan was to utilize the three 9 kWh Sunverge Li-ion bundled systems to function in a manner analogous to a utility grid backing up a grid-tied solar PV system. The systems could also serve new opportunity loads (load dumps) once the primary batteries reached full capacity and went into float mode. The opportunity loads comprised of a new 40 gallon domestic water heater to serve the kitchen area and a new dedicated circuit with a power outlet installed in the kitchen to serve a small water distillation system or a countertop ice machine.
This approach involved allocating battery storage into two partitions: a primary storage bank using the existing Outback and a combination of existing lead-acid and new absorbed glass mat (AGM) batteries, plus an additional secondary back-up bank using the donated energy Li-ion storage systems. The site load would then be served by the primary bank on most typical, low-use days. The secondary bank would back up the primary system on higher demand days and would otherwise serve the new opportunity loads when excess power could be generated.

However, once tied into KHM, the Sunverge units proved to be problematic due to overnight inverter standby losses that lost 67% of the battery energy gained during the day. Additionally, the Sunverge units were designed to interconnect with a utility grid as backup when their own batteries were depleted. Sunverge technicians communicated that in a completely off-grid environment, the batteries would emulate grid support (backup) to the primary battery source serving the site load. However, in standby mode, the Sunverge grid interface controls would continually send out pulses to sense line loads that would signal its internal auto transfer switches to engage the system when primary power is lost. These pulses were picked up by the new external electro-mechanical auto transfer switches that connected the two storage systems and it was found they were not compatible.

The KHM power system attempted to auto switch between the primary “Outback” power system and the Sunverge units, but failed as a result of the conflicting protocols of the internal and external auto transfer switching systems. The incompatibility of the built-in Sunverge control systems with the system’s controls deemed it necessary to disassemble the Sunverge units to salvage the Li-ion batteries, discarding the incompatible bundle of inverter, charge controller, and related on-board controls and relying upon the new central control scheme to manage load and storage distribution.

Subsequently, the design approach was modified to partition the storage into primary and secondary storage. The primary battery storage partition consisting of the existing Outback inverters and controller, the existing bank of AGM batteries, and 12 of the site’s 24 PV panels dedicated to that sub-system. A second inverter by Sungold was added to feed the salvaged Li-ion batteries, serving as the backup. The “Sungold” backup system was to serve as an instantaneous “spinning reserve equivalent” that would be automatically triggered when the Outback system was depleted.

We subsequently concluded that the Sungold backup power remaining continuously online as an instantaneous “spinning reserve equivalent” was inefficient, which lead to another significant shift in approach.

**Inclusion of a Supply-Side Management System**

Due to high inverter standby loss issues, the project then evolved once more from a purely load-side management system (in which dump loads were to be added to utilize excess generation) to
include a *supply-side* management system that incorporated the new opportunity/dump loads, but also strategically managed the deployment of battery power to minimize standby losses and increase reliability. The team then developed “predictive look ahead programming,” an approach that utilizes programmable electronic automatic transfer switches (ATS) and voltage sensing relays to activate the backup system prior to full discharge and disconnection of the primary bank. A brief overlap of both systems allows for a seamless, high-speed, no-blink transfer of battery banks, analogous to a utility power plant maintaining spinning reserve. This solution enables the Sungold inverter to remain OFF, rather than in standby mode, and be automatically powered up shortly before the load is transferred from the primary Outback system. Details of the control strategy and control design are described in detail in HNEI’s internal report on the project, which is available on HNEI’s website at [https://www.hnei.hawaii.edu/publications/project-reports/aprises-16/](https://www.hnei.hawaii.edu/publications/project-reports/aprises-16/).

As described in the full report, by integrating programmable and voltage sensing auto transfer switches with electro-mechanical ATS and adding new opportunity load dumps that are isolated from the primary and backup supply sources, the KHM small off-grid system was able to capture more of the solar energy with fewer power interruptions and provides new qualitative services on site. Predictive look ahead programming also eliminated unnecessary standby losses. Battery partitioning provided a solid backup (spinning reserve) for the primary battery system.

**Adaptive Lighting for Energy Efficiency and Security**

Under this activity, HNEI collaborated with the California Lighting Technology Center at the University of California, Davis to demonstrate and test a prototype adaptive lighting system intended to save energy and provide additional security in an outdoor setting. Demonstrations were established at two sites, at the University of Hawai‘i at Mānoa and at a civilian U.S. Navy facilities site. A technical report describing the project details and key findings is available on HNEI’s website.

While it is difficult to quantify the precise quantity due to rapid changes in technology and adoption, a 2012 Department of Energy study indicated approximately 17% of all U.S. lighting energy used can be attributed to outdoor lighting [1]. In most cases, outdoor lighting fixtures operate through the night at fixed illumination and power levels and are traditionally operated by programmable digital and mechanical timers to turn the fixtures on and off. Advancements in lighting control and sensing technologies have led to a control approach to modulate lighting and power levels to meet the requirements of a specific building environment.

*Adaptive lighting* integrates advanced sensing devices to detect motion during select programmed periods of the day, in order to activate a change in light level from a fixture or network of fixtures only when human motion is detected in the area. The adaptive lighting approach to system design significantly reduces the energy load, which enables fixtures to reduce their output from 100% power, down to as low as 20% when there is no activity in the area and no requirement for
continuous full power. Adaptive lighting has become a best practice for outdoor lighting in many jurisdictions and has been included in various building energy codes. However, the public perception that a bright, well-lit area is less susceptible to crime results in wasted energy in order to maintain a uniform and potentially unnecessary light level.

Adaptive outdoor lighting systems utilize a meshed network of photo sensors to detect ambient daylight levels control the electric light source and motion sensors to detect when a space is occupied/vacant. In most adaptive lighting cases, outdoor fixtures that operate at full power at night automatically reduce light levels when there is no activity in the defined area and prescribed times. A motion sensor detecting unexpected motion sends a signal that triggers the lighting system to increase the output of the networked fixtures to a maximum light level. The power reduction from maximum to the lower light setting saves energy while providing enough light to meet minimum end-use safety requirements.

A secondary aspect of adaptive lighting systems is not related to energy savings, but to security applications. Research has indicated that the perception that a bright, well-lit area is less susceptible to crime may not always hold true. In 2002, a study conducted by Clark [2] showed that high, uniform light levels have little to no deterrent effect on crime; rather, the elevated levels of illumination typically only increase the perception of security for people using the space. Thus, a significant amount of energy may be wasted when over-lighting an outdoor space at a constant and potentially unnecessary light level. However, when the outdoor illumination from the network of outdoor lighting instantly increases from say 20% to 100%, the highly visible “surprise” will effectively serve as an alarm to security guards or others, that an intruder has encroached on the property.

This project had four key objectives:

1) Identification and testing of adaptive outdoor lighting system technologies;
2) Prototyping of an adaptive, sensor-based lighting system appropriate for use in security applications;
3) Validation of the concept through installation of the prototype system in a campus setting; and
4) Demonstration of the system in two real-world security applications on a naval base.

This project was intended to demonstrate potential energy savings from the lighting reduction, as well as collect feedback from building users that may have observed the pre- and post-conditions. For this proof-of-concept demonstration project, two locations in Honolulu, Hawai‘i were selected for field implementation. Four total systems were installed: two on University of Hawai‘i at Mānoa (UHM) FROG buildings (Figures 7.1.3 and 7.1.4) and two located on the grounds of NAVFAC Hawai‘i (Figure 7.1.5).
The California Lighting Technology Center (CLTC) vetted several outdoor sensors and networked lighting control systems, including a dual technology, passive-infrared sensor, a solid-state Light Detection and Ranging (LiDAR) sensor, and two mechanical LiDAR sensors. CLTC tested detection range and spatial sensitivity for the sensors and concluded that the two mechanical LiDAR sensors (Optex RLS-2020s and Optex RLS-3060) outperformed the other two types in
terms of reliability and consistency in detection. The existing exterior light fixtures on the test locations were replaced with the LED fixtures with dimming capabilities. Deco D464 fixtures were installed on the two UHM FROG buildings and NAVFAC Building MP3 and a RAB FFLED18 fixture was installed on the NAVFAC guard shack. Each system also incorporated a Hubbell Gateway 3 wireless controller using Hubbell WIR REM-L Wireless nodes installed on each light fixture to connect the fixtures and the sensors into a single mesh network, which allowed all fixtures to activate, dim, and recover synchronously.

Power usage data to the UHM FROG buildings was collected using Continental Control Systems current transformers to an Ezesystem ezeio data logger. Metering equipment was installed on the NAVFAC sites to monitor pre- and post- lighting energy consumption. WattNode RWNB-3Y-208-P power and energy meter collected the data, Continental Control Systems current transformers were installed on the circuit breakers, and a HOBO UX120-017M data logger stored the data.

To determine energy savings, pre-retrofit baseline power data was collected from September through mid-December 2019. Upon completion of the retrofit, data was collected from late-December 2019 through July 2020.

To extrapolate annual energy savings, HNEI and CLTC gathered historic data associated with the daily sunrise and sunset times for the area over the monitoring period through publicly available weather monitoring sites. Each associated nightly length and recorded nightly energy use was then scaled and averaged over the recorded period for each phase. Then using the average of those scaled values, an approximate yearly energy use curve was created to extrapolate the estimated annual energy savings during each stage.

At the UHM FROG buildings, two Optex 3060 sensors with a 180° field of view and three Optex 2020 sensors with 90° field of view were installed to capture 100% of the area surrounding the two buildings (Figure 7.1.4).

Based on the normalized data collected at UHM FROG 1 and 2, annual energy savings achieved by adding the LiDAR occupancy sensor to a LED wallpack with a photocell is estimated at approximately to 16.8% (Table 7.1.1). This is an additional 4.3% to 8.7% energy savings as compared to the LED wallpack paired with only a photocell at the same installation. Additional discussion of the results can be found in the full report on HNEI’s website.
Table 7.1.1. Energy use savings comparisons for UHM FROGS 1 and 2.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>FROG 1</th>
<th>FROG 2</th>
</tr>
</thead>
<tbody>
<tr>
<td># of Days Monitored</td>
<td>13</td>
<td>79</td>
</tr>
<tr>
<td>Total Energy Use for Monitored Period (kWh)</td>
<td>61.3</td>
<td>40.8</td>
</tr>
<tr>
<td>Length-of-Day Adjusted Average Daily Energy Use (kWh)</td>
<td>1.37</td>
<td>1.28</td>
</tr>
<tr>
<td>Length-of-Day Adjusted Annual Energy Use (kWh)</td>
<td>501.4</td>
<td>466.0</td>
</tr>
<tr>
<td>Calculated Annual Energy Savings vs. LED Wallpack (%)</td>
<td>-</td>
<td>7.3%</td>
</tr>
</tbody>
</table>

At NAVFAC Hawai‘i, two sets of sensors (one Optex 3060 and one Optex 2020) were installed: one set to capture the parking lot side and the main entry of Building MP3 and one set on the guard shack, which allowed for coverage on the primary points of entry (Figure 7.1.5).

Based on the normalized data collected at Building MP3 and the south guard shack, annual energy savings achieved by adding the standalone LiDAR occupancy sensor to an LED wallpack in military applications is estimated to range between 36.1% to 44.3% (Table 7.1.2).

Table 7.1.2. Energy use savings comparisons for NAVFAC Hawai‘i Building MP3 and the guard shack.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Building MP3</th>
<th>South Guard Shack</th>
</tr>
</thead>
<tbody>
<tr>
<td># of Days Monitored</td>
<td>90</td>
<td>224</td>
</tr>
<tr>
<td>Total Energy Use for Monitored Period (kWh)</td>
<td>119.3</td>
<td>180.3</td>
</tr>
<tr>
<td>Length-of-Day Adjusted Average Daily Energy Use (kWh)</td>
<td>1.26</td>
<td>0.81</td>
</tr>
<tr>
<td>Length-of-Day Adjusted Annual Energy Use (kWh)</td>
<td>461.6</td>
<td>294.3</td>
</tr>
<tr>
<td>Calculated Annual Energy Savings vs. LED Wallpack (%)</td>
<td>-</td>
<td>44.3%</td>
</tr>
</tbody>
</table>
In order to determine the perception of visual impact from the adaptive systems, CLTC disseminated surveys to users of the sites. With a small sample of respondents from each site, 17 in total, it made it difficult to reach firm conclusions regarding impressions of the absolute impact, light quality, and how noticeable was the change in light level; of the respondents that offered an impression, 47% cited their overall impressions as positive and 24% were neutral. There were no negative impressions.

This project demonstrated that energy savings ranging from 16% to 44% were achievable by adding sensitive LiDAR motion detecting technology to dimming LED fixtures in a networked environment. Lesser savings were observed at the UHM FROG sites because they were originally equipped with efficient LED fixtures with photocells and PIR motion detecting, bi-level modes of operation. LiDAR installed on those buildings allowed for only a modest 4.3% to 8.7% improvement. Originally equipped with LED exterior fixtures with photocells, but no bi-level capabilities, the NAVFAC buildings had a greater potential for energy savings when adding the LiDAR motion detectors.

Based on research from this project and other similar work, a number of recommendations on general security exterior lighting specification are proposed (Table 7.1.3). These recommendations are also discussed in greater detail in the full report.

Table 7.1.6. Recommendations for general security exterior lighting system specifications.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Recommendation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Distribution</td>
<td>Full cutoff, or U0 in the BUG classification system</td>
</tr>
<tr>
<td>Dimmability</td>
<td>0-10V to enable bi-level functionality</td>
</tr>
<tr>
<td>Color Rendering Index</td>
<td>80 or greater</td>
</tr>
<tr>
<td>Correlated Color Temperature</td>
<td>3,000 K or less</td>
</tr>
<tr>
<td>Connection Type</td>
<td>ANSI 7-pin</td>
</tr>
<tr>
<td>Lighting Level</td>
<td>Meet DOD criteria for location’s specified level of protection</td>
</tr>
<tr>
<td>Occupancy Sensor</td>
<td>Compatible with lighting system controls; reliable detection of occupants</td>
</tr>
<tr>
<td>Dusk-to-Dawn Operation</td>
<td>Photocell or timer clock schedule</td>
</tr>
<tr>
<td>Cybersecurity</td>
<td>Comply with site networking requirements to ensure cybersecurity system; standalone systems with no networking components are compliant at most DOD sites.</td>
</tr>
</tbody>
</table>

References


7.2 Electrified Transportation

As an alternative to the original planning study (volume and flow of electric transportation options between UH and DoD bases), an analysis was conducted to assess the impact on fossil fuel use and emissions with the transition from Internal Combustion Engine (ICE) to plug-in Electric Vehicles (EVs), in combination with renewable electricity generation on a remote, isolated power grid. A database and spreadsheet model were developed to calculate the impact of this transition on the highly oil-dependent Island of O‘ahu, Hawai‘i. Detailed fossil fuel use and resulting emissions were calculated for 2017 through 2020, based on publicly available data. Passenger and freight vehicles were assessed, powered by gasoline, diesel, and electricity. In 2020, average passenger EVs consumed seven times less fossil fuel compared with gasoline-powered passenger vehicles and cut CO₂ emissions in half. Using published projections for EVs replacing ICE vehicles and renewable electricity generation replacing fossil fuels, four scenarios were modeled and assessed out to 2050. Results show fossil fuel use and CO₂ emissions plunging with more clean power and decreasing ICE numbers. With the most ambitious scenario modeled in this study, with the faster rate of EV adoption combined with the faster projection for renewable power generation on O‘ahu, 99% less fossil fuel is expected to be consumed for all passenger and freight vehicles, and 93% less CO₂ emitted between 2020 and 2050. With the slower projection for EV adoption, fossil fuel use and emissions from ICE vehicles persist, consuming billions more gallons of gasoline and generating tens of millions more tons of CO₂. Complete details on the research can be found in the peer-reviewed journal publication listed below.

Additionally, under this APRISES16 funding, the task lead served on the Hawai‘i Climate Change Mitigation and Adaptation Commission’s advisory group on reduction of ground transportation emissions. News releases written for SOEST and UH, and the journal publication were picked up by The London Daily Mail, EurekAlert! (American Association for the Advancement of Science), The Garden Island, Electronics 360, The Washington Time, and Maui Now. Interviews were also conducted with the Honolulu Star Advertiser resulting in a front-page article and editorial, and ThinkTech Hawai‘i livestream interview and presentation.
Publications and Presentations

Peer-Reviewed Publications


Conference Proceedings and Presentations


Interviews