FINAL TECHNICAL REPORT

Executive Summary

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EXECUTIVE SUMMARY

This report summarizes work conducted under Grant Award Number N00014-21-1-2250, the Asia Pacific Research Initiative for Sustainable Energy Systems 2020 (APRISES20), 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 APRISES20 comprises research, development, testing, and evaluation (RDT&E) over a range of technical areas. These include Electrochemical Technologies with a focus on fuel cells and batteries; Alternative Fuels including carbonization of biomass and hydrogen technology; Resilient Energy Systems including development and demonstration of novel technologies for advanced smart microgrids and resource adequacy studies for the Hawai‘i electrical grids; and Advanced Materials for energy applications including novel metal containing ionic liquids capable of contaminant removal under harsh environmental conditions and printable polymer composites for photovoltaic and other electronic applications. Makai Ocean Engineering, under subcontract to the University of Hawai‘i, also continued their efforts to develop high-performance, low-cost heat exchangers. A stop-work order terminated this grant prior to the initial end date, which limited the completion of a portion of the work proposed and planned. A brief summary of results from the completed work, by major task follows.

Task 1, Program Management and Outreach, supported senior faculty and project support personnel responsible for overall program management and coordination, development and monitoring of partner and subcontract agreements, and preparation of reports and outreach materials for ONR and other stakeholders.

Task 2, Electrochemical Technologies, included RDT&E in the areas of fuel cells and batteries.

Under Subtask 2.1, Fuel Cell Testing and Development, HNEI's research encompassed five activity areas: a) analyzing recovery procedures for fuel cells exposed to contaminants; b) development of a novel layered inorganic material for the catalyst layer for high temperature proton exchange membrane fuel cells; c) advancements in materials to enable both in-situ and ex-situ strategies for fuel cell contaminant mitigation and performance enhancement; d) a study of the approach to calibrate reference electrodes experimentally to the reversible hydrogen electrode

scale for standardization; and e) exploratory research into the modification of a PEMFC for catalytic cogeneration of hydrogen peroxide and electricity. Each of these are summarized below.

2.1a) Broad application of proton exchange membrane fuel cell (PEMFC) technology will require enhanced durability to ensure reliability of fuel cell operation in real-world environments. The sensitivity of PEMFCs to operating and environmental conditions is a serious issue since impure fuel or oxidizer negatively affects performance and compromises the reliability of fuel cells. Since ambient air is used as an oxidant, PEMFCs are susceptible to airborne contaminants. This work was intended to analyze potential recovery procedures for PEMFCs exposed to SO_2 in the air stream and evaluate their efficiency under varying operating conditions. Results suggest that while both potential cycling and O_2 purge technique recovery methods are effective, the latter is more practical for field applications due to its simplicity and lack of need for auxiliary equipment. Details of this work was published in the *Electrochimica Acta* journal and presented at a conference.

2.1b) HNEI continued to look at fundamental issues related to the development of robust and durable fuel cell power systems (FCPS) capable of operating in harsh environments. Recently, with the development of high temperature proton conductive electrolytes for the catalyst layer, H_3PO_4 doped PBI (H_3PO_4/PBI) has been identified as one of the approaches for high temperature (HT)-PEMFCs. Under this activity, HNEI has been developing a new layered inorganic material to replace H_3PO_4/PBI for the catalyst layer of HT-PEMFCs, to address the concerns of the application temperature limit of perfluorosulfonic acid (PFSA, Nafion®) polymer electrolytes (a typical PEM), and overcome the phosphoric acid leaching issue of the H_3PO_4/PBI (a promising and widely studied HT-PEM for membrane and electrolyte in the catalyst layer). Microscopy, spectroscopy, and diffraction analysis, as well as water solubility and stability tests were conducted. The latest developments are presented in further detail below.

2.1c) As part of the continued exploration into technologies to enable operation of fuel cells operating on ambient air in harsh environments, HNEI explored the development of an in-situ catalytic conversion layer to remove contaminants before they reach Pt catalyst. The particle size and loading of the contaminant-active catalysts, the composition, and structure of in-situ catalytic conversion layer can be optimized to minimize transport resistance, and maximize catalyst utilization, contaminant removal efficiency, and the contaminant tolerance of MEA in PEM fuel cells. Contaminant-active catalysts based on transition metal carbides were synthesized and the electrochemical oxidation of aqueous SO_2 at transition metal carbides catalysts was initially evaluated by ex-situ cyclic voltammetry in acidic medium. A potential candidate material for selective oxidation of SO_2 was identified for integration into a single cell fuel cell.

2.1d) Efforts under this activity focused on continued advancement of advanced diagnostics for the study of fuel cells. This work studied the approach to calibrate reference electrodes experimentally to the reversible hydrogen electrode (RHE) scale. Various working electrodes,

rotation rates, scan ranges, and scan rates were carried out to demonstrate how the calibration process would affect the calibrated RHE values of reference electrodes. This experimental practice aims to benefit the standardization of experimental reference electrode calibration in the electrochemical field. Details of this work will be submitted for publication in a peer-reviewed journal.

2.1e) Hydrogen peroxide is widely used as an environmentally friendly bleaching agent, disinfectant, and oxidizer for industry, as well as the military. The main method for hydrogen peroxide production today, an anthraquinone oxidation process, is not ideal as it is energy intensive, expensive, not environmentally friendly, and only allows for large scale operations. Hydrogen peroxide is a strong oxidizer and can be very corrosive and even explosive when transported in bulk from the production site to the point of use. Because of these safety concerns, hydrogen peroxide is not readily accessible in developing countries where they would greatly benefit from the water treatment. Under this activity, HNEI developed a new approach to the production of hydrogen peroxide by shifting the cathode reaction which produces water, to selectively produce hydrogen peroxide while still generating electricity. Details of this work was published in a Master of Science thesis.

Under Subtask 2.2, Battery Characterization and Modeling, HNEI research covered three main topics: a) the evaluation of commercial sodium-ion batteries, b) the characterization of the relationship between the impact of rate and temperature, and c) the continuation of the development of our modeling framework with the validation and implementation of new features.

2.2a) HNEI collaborated with RWTH Aachen University, Germany, Sandia National Laboratories, and the University of Oviedo in Spain to evaluate the cell-to-cell variations, the cycling performance, and the diagnosability of three different batches of commercial Na-ion cells containing a hard carbon negative electrode and a nickel, iron, and manganese layered oxide positive electrode. Results indicated similar cell-to-cell variations compared to Li-ion batteries, but much lower cycle life. Moreover, the degradation mode approach was found to be applicable to sodium-ion batteries. Details of this work was published in the *Batteries & Supercaps* journal, presented at a conference, and another manuscript was submitted for publication in the *EES Batteries* journal and is currently under review.

2.2b) HNEI focused on the emulation of the impact of temperature using data at different rates. On-board battery diagnosis accuracy can be significantly affected by the cells temperature that will affect the cells' voltage and thus some of the information fed to the battery management system. To circumvent this problem, we investigated the relationship between the impact of rate and the impact of temperature on the electrochemical response of two commercial Li-ion batteries. We studied the relationship between rate and temperature to define a simple set of equations enabling the emulation of the electrochemical response of the cells at different temperature without the need

for any battery model. Details of this work was published in the *Journal of Power Sources* and presented at a conference.

2.3c) HNEI collaborated with the University of Warwick, UK, and with the Offenburg University, Germany, to implement new features into our modeling framework. With Warwick, HNEI developed a novel silicon-specific diagnostic marker for the detection of silicon active material loss. The proposed method was validated using synthetic datasets generated from the ʻalawa mechanistic modelling toolbox, simulating a broad range of degradation mode combinations and cell architectures. With Offenburg, HNEI proposed a physically-informed equivalent circuit model directly integrating key degradation modes (loss of active material at positive and negative electrode, and loss of lithium inventory). The rate expressions for each aging mode included a calendric component (dependent on half-cell potential) and a cycle component (dependent on current and relative volume changes in the active materials), which allowed to describe well the degradation of commercial Li-ion cells under complex duty cycles. Details of this work was published in two papers in the *Journal of the Electrochemical Society* and presented at a conference.

Under **Task 3**, HNEI continued research in two areas: constant volume carbonization of biomass and hydrogen refueling technology. Under Subtask 3.1, Constant Volume Carbonization, HNEI investigated the impact of pressure and oxygen content on the auto-thermal pyrolysis of woody biomass. Details of this work formed the basis for a U.S. provisional patent and will be published in the *Energy and Fuels* journal. HNEI continued research, development, demonstration, and assessment of hydrogen production, storage, and dispensing systems for heavy duty hydrogen vehicles, and evaluation of the operational performance of buses on the Big Island of Hawaiʻi under Subtask 3.2. The team resolved critical technical issues with the hydrogen fuel cell buses, advanced daily bus operations, completed commissioning of the hydrogen refueling station, and installed performance monitoring systems. Various workforce training and outreach engagements were supported by APRISES20 funds as well.

Under **Task 4**, Resilient Energy Systems, HNEI continued research to enable the development of resilient, reliable, and secure energy systems operating with a high penetration of variable renewable generation technologies. Hawaiʻi's energy and economic security requires continued reduction of the importation of fossil fuel supplies. With options for firm renewable energy resources limited, advancing renewable energy targets is increasingly dependent on integrating exceptionally high penetrations of wind and solar energy. Similar issues exist on other Pacific Islands and areas of interest to DOD.

The research included two closely integrated activities. Under Subtask 4.1, HNEI continued development of enabling technology focused on the integration of new technology and reliable control at the grid edge. Subtask 4.2 was intended to focus on power systems analysis to ensure that the energy systems and related critical infrastructure on Oʻahu and the other Hawaiian Islands,

home to the Pacific Command and the largest military bases in the Asia Pacific region, meets the reliability, security, and resiliency needs of DOD as additional variable generation technologies are integrated into the grid. This activity leverages resources from the Energy Systems Development Special Fund (ESDSF) managed by HNEI (also known as "barrel tax"). Due to early termination, much of this effort was shifted to the ESDSF.

Subtask 4.1, Advanced Grid Technology, focused on developing, testing, and demonstrating innovative technologies and strategies to enhance grid reliability and performance through the integration of advanced control systems and laboratory infrastructure. Led by HNEI's Grid System Technologies Advanced Research Team (Grid***START***), this effort built on previous work by advancing practical methods and enabling technologies to support electric vehicles (EV) integration and microgrid research. The work emphasized solutions for bidirectional EV charging, energy management optimization, and establishment of Advanced Power System Laboratory (APSL) to facilitate rigorous testing, validation, and training in advanced power system technologies.

4.1a) HNEI, in collaboration with IKS Co., Ltd. ("IKS"), continued advancing the development, testing, and demonstration of advanced control systems for bidirectional EV chargers deployed at the University of Hawai'i's Mānoa campus. The team has been creating, assessing, and demonstrating new algorithms designed to efficiently manage EV charging and discharging cycles, with the goal of minimizing overall energy costs for shared fleet vehicle operations. Significant progress was made. The project focused on enhancing and continuously monitoring an EV charging management system to maximize fleet utilization and optimize charge/discharge schedules. The team developed detailed mathematical models to accurately calculate electricity bills for various Hawaiian Electric Company's time-of-use rate schedules, and analyzed actual charging and discharging data to refine optimization algorithms. Minimum driving range thresholds were established for each vehicle, helping to balance cost savings with daily transportation needs and reduce driver "range anxiety." Machine learning methods were applied to improve EV energy consumption estimates, resulting in more precise energy management. Project findings and outputs, including a model assessing fast EV charger integration into low-voltage networks, were presented at an IEEE conference. The initiative also provided hands-on training for engineering graduate and undergraduate students, equipping them with practical skills in system optimization and troubleshooting.

4.1b) The completion of the APSL represents a major achievement under APRISES20. Located at the University of Hawai'i Marine Center, the APSL provides a flexible, state-of-the-art environment for hands-on research into grid integration, microgrids, and advanced energy technologies. The facility features a 35.3 kW rooftop PV, multiple advanced inverters, modular AC/DC equipment test bays, and a 600 V_{CD} off-grid test bed, as well as a real-time grid simulator supporting power hardware-in-the-loop (PHIL) testing. Built with strong safety measures, including arc-flash protected Meltric receptacles and emergency shutdown systems, the APSL

enables rigorous evaluation of next-generation grid devices and control strategies. Since its completion, the laboratory has been used to validate solutions for projects such as the advanced conservation voltage reduction demonstration project in Okinawa, Japan (another ONR funded project), and to provide advanced training for local and international engineers, positioning it as a key resource for ongoing energy innovation in Hawai‘i and beyond.

Under Subtask 4.2, Resilient Grid Systems, HNEI focused on support of development efforts for the Moloka‘i Community Energy Resilience Action Plan (CERAP) and developed a paper study to examine the potential for various electro-fuels to support the islands' firm power needs. The latter is available as a draft, but cannot be considered final as the award was terminated before references were validated. Reliability studies initiated under APRISES19 were deferred to APRISES 21.

Task 5, Advanced Materials, comprises two subtasks that includes research on novel metal containing ionic liquids capable of removal of acidic gas contaminants (SO_2) from air and advancing photovoltaic (PV) technologies by developing printable thin-film solar cells.

Under Subtask 5.1, Purification Technology, HNEI staff synthesized three novel metal-containing ionic liquids (MIL): $Zn_3[OAc]_8[C_2mim]_2$, $Mg_4[OAc]_{10}[C_2mim]_2$, and $Fe_4[OAc]_{10}[C_2mim]_2$, and characterized their properties. The best-performing sorbent, $Mg_4[OAc]_{10}[C_2mim]_2$ impregnated onto activated carbon, had an SO_2 breakthrough capacity of 215 mg SO_2/g MIL, which was comparable to the state-of-the-art [C_2mim] [OAc] ionic liquid impregnated onto activated carbon. Results from this work indicated that metal-containing ionic liquids are good candidates for practical acidic gas mitigation at low contaminant concentrations. Details of this work was published in two papers in the *ACS Omega* journal and a Master of Science thesis.

Under Subtask 5.2, Printable Electronic Materials, the research team at HNEI's Thin Films Laboratory aimed to advance low-cost, scalable photovoltaic (PV) technologies by developing printable thin-film solar cells based on chalcopyrite $CuInSe_2$ (CISe) materials. These materials offer a promising alternative to rigid silicon PV modules, especially for portable and wearable applications where flexibility and lightweight design are crucial. Leveraging earlier work funded by ONR, researchers formulated a stable, non-toxic molecular ink to fabricate CISe absorbers via solution processing, achieving conversion efficiencies exceeding 8%.

A key innovation of this project was the incorporation of aluminum salts into the CISe ink to enable in situ formation of nanoscale Al_2O_3 during processing. This approach eliminates the need for vacuum-based post-deposition treatments typically used for surface passivation. The addition of Al_2O_3 was shown to significantly improve solar cell performance. Systematic variation of the aluminum content revealed that moderate levels (e.g., Al-20) produced absorbers with improved morphological features and a higher density of passivating particles, leading to power conversion efficiencies up to 11.2% in champion devices and average values as high as 9.5%.

Further electrical characterization confirmed that Al_2O_3 inclusion reduced defect densities, increased the space charge region width, and shifted the dominant recombination mechanism from interface to bulk. Temperature-dependent open-circuit voltage measurements supported these findings, showing activation energies closer to the bulk bandgap in Al-doped films. Together, these results demonstrate the effectiveness of aluminum doping and in-situ Al_2O_3 passivation in enhancing CISe solar cell efficiency and underscore the viability of low-cost, ink-based manufacturing for next-generation photovoltaic technologies.

Under **Task 6**, Advanced Heat Exchanger Development, Makai Ocean Engineering continued to develop their Thin Foil Heat Exchanger (TFHX™) with increased emphasis on designs to provide a path to commercialization. A key accomplishment during this period was development of new fabrication techniques to reduce weld failure. An automated, self-cleaning system has been in operation for one year. Maximizing plate area in single housing was identified as a key requirement to meet cost targets. Various pressure rated housing designs were evaluated for operations and ease of maintenance. Makai developed new methods for stacking of the plates for large areas designs. Makai also developed techniques, fixture designs, and equipment to improve serviceability for mitigation of biofouling. Details of this work is available in Makai's report.

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 noted below and available on HNEI's website at https://www.hnei.hawaii.edu/publications/project-reports/aprises-20/.**