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# University of Hawaii at Manoa

Hawaii Natural Energy Institute  
Holmes Hall 246 • 2540 Dole Street • Honolulu, Hawaii 96822

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Mr. Neil P. Rossmeissl  
Office of Energy Efficiency and Renewable Energy  
U.S. Department of Energy  
1000 Independence Ave.  
Washington, D.C. 20585

Progress Report for Grant No. DE-FG36-94AL85804

VIA FAX: 202 586-0784, Total pages- 8, Original hard copy to follow

Dear Neil:

Attached is a summary of progress under our "Hydrogen from Renewable Resources" grant for December 1995. The thermodynamic characterization of the solid-gas behavior of the polyhydrides is back in with the most recent progress included in this report.

I understand from Oskar that you have the photobiology proposal in hand and assume you also received our white paper for a bench-scale gasification effort. I had intended to call last week but was out of the office several days. I will give you a day or two to recover from the snow and will then try you to discuss both of these items. I am also trying to get our fiscal people moving a little quicker on the invoicing. Hopefully I'll get somewhere now that the holidays are over.

Hope your holidays were enjoyable.

Sincerely,

Richard E. Rocheleau  
Principal Investigator

cc: Catherine Gregoire Padró  
Doug Hooker - via fax 303 275 - 4753  
DOE Office of Scientific & Technical Information  
HNEI fiscal

MASTER

# MONTHLY PROGRESS REPORT

Hydrogen from Renewable Resources  
University of Hawaii  
Grant No. DE-FG36-94AL85804

December 1995

## TASK 1. HYDROGEN PRODUCTION

### Subtask A. Thermochemical Production of Hydrogen from Wet Biomass - M. J. Antal

This month, we enjoyed the cooperation of two visiting researchers: one stayed with us for one month, and the other will work with us till next March. We also now have a visiting student who will stay with us for five months. With a help of these new co-workers, who are working free of charge to our DOE contract, two main achievements were made: 1. Design of the feeder section for a new reactor which accommodates feeding of a slurry of high concentration was completed. 2. The effectiveness of gas-liquid separation under a high pressure to obtain hydrogen of a higher purity was ascertained both theoretically and experimentally. Also, an oral presentation "Thermochemical Conversion of Wet Biomass to Gaseous Fuel in Supercritical Water" was made at the International Chemical Congress of Pacific Basins Societies, Honolulu, Dec. 17-22, 1995.

**1. New Reactor/Feeding System Design:** The conceptual design of the scaled-up reactor and biomass feeder has been completed. No welding parts will be used in the reactor system. The feeder will consist of a piston and a pressurized vessel with a coned bottom which will make it easier for the biomass slurry to flow. The feeding system is designed to feed high concentration biomass slurries.

**2. Gas-Liquid Separation Under a High Pressure:** We proposed gas-liquid separation under a high pressure (34.5 MPa), where most of the carbon dioxide is expected to be present in the liquid phase, and thus the gas phase will be mostly composed of hydrogen. This system may eliminate or reduce the load of the hydrogen-carbon dioxide separator, which is to be placed downstream of the supercritical water gasifier. We determined the effectiveness of this high-pressure separation by both experimental and theoretical methods. A rough estimation using the solubility data of hydrogen and carbon dioxide showed only one seventh of the produced carbon dioxide is dissolved in the liquid phase. Thus, we proposed a new idea that additional cold water should be supplied to the effluent exiting the reactor so that carbon dioxide can be dissolved to a higher extent. To obtain 95% pure hydrogen, 20 part of additional water should be used for 1 part of effluent under 34.5 MPa. The power required for compression of water is less than 1% of the heat required to increase the temperature of the feedstock. This effect was also ascertained by experiment. Glucose solutions of 2, 1, and 0.5 M were gasified in the H<sub>2</sub> reactor and effluent gas was sampled at both 34.5 MPa and 0.1 MPa. For 2 M glycerol solution, the ratio of carbon dioxide concentration to hydrogen concentration varied from 0.35 to 0.21, indicating more carbon dioxide dissolved in liquid phase, when we changed the

sampling method from low-pressure to high-pressure sampling. This tendency is more evident for the 0.5 M solution, where the amount of water is larger for a specific effluent gas generation. This carbon dioxide-hydrogen ratio decreased from 0.58 to 0.11 for the corresponding change of sampling method.

**3. Future Work:** In January, 1996, a heat transfer calculation will be made to determine the size of the reactor. The parts for the reactor and feeder will be ordered. As for high-pressure gas-liquid separation, a more precise calculation for the composition of each phase at high pressure will be conducted through the calculation of fugacities. Some additional experiments will be also conducted, and we will write a short paper on this subject.

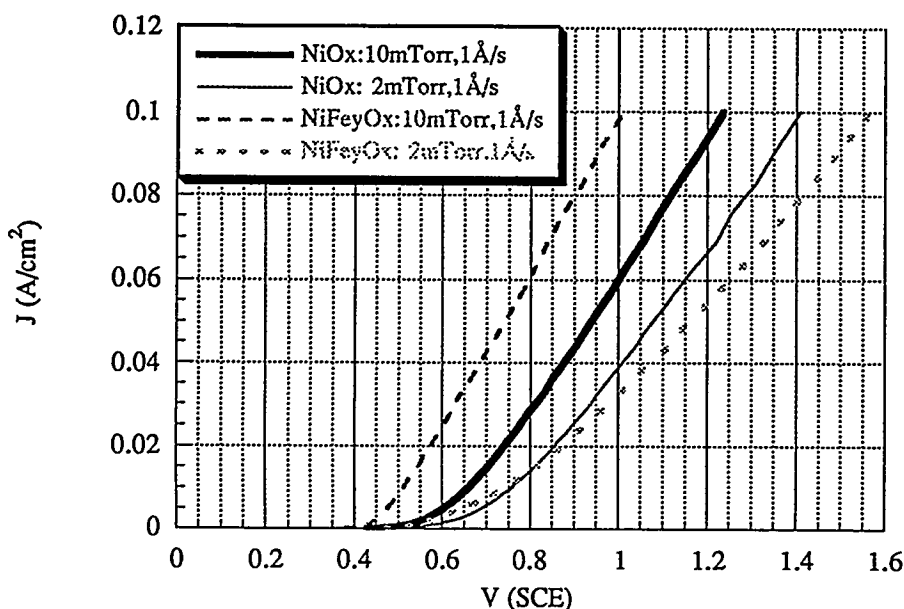
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## Subtask B. Photoelectrochemical Production - R. E. Rocheleau

Characterization of the electrochemical, optical and compositional properties of the sputter-deposited nickel-oxide and nickel-iron-oxide films discussed in previous reports has been completed. As described in past months, the oxygen catalysis of these films is strongly dependent on film composition and on deposition conditions. This is illustrated in the figure below which shows the large-current behavior of representative  $\text{NiO}_x$  and  $(\text{NiFe}_y)\text{O}_x$  films deposited at pressures of 10 and 2 mTorr. The catalytic responses are significantly different with the 10mTorr  $(\text{NiFe}_y)\text{O}_x$  exhibiting the lowest overpotentials. We are currently attempting to interpret the results in terms of both the electrochemical exchange current density and solid-state film bulk and contact resistances. A full tabulation of the completed electrochemical, optical and composition test results, which is currently underway, is providing important insights.

J-V Catalysis Plots for Sputtered  $\text{NiO}_x$  and  $\text{NiFe}_y\text{O}_x$  Films



The long-term stability of these catalyst films in alkaline solution remains of great interest for use in PEC cells. Two new Plexiglas cells with a cathode-to-anode separations of approximately 1-inch have been completed. Per previous reports, the new design uses Teflon seals to isolate the active areas and allows simultaneous collection of both oxygen and hydrogen with no dead volumes which can trap gas. The cells also have provision of inserting a 3/8" SCE electrode symmetrically to both electrodes for monitoring the half cell potentials. Initial long-term testing is planned for January 96. The same cells will be used for long-term testing of the photoelectrodes fabricated from our remaining multijunction cells.

A literature search was conducted to update conditions for deposition of high quality boron-doped and intrinsic a-SiC:H films and for comparison of our results to date. For boron-doped films, our data were found to be consistent with that in the literature in terms of growth rate, band gap, and conductivity. Due to the variability from system to system and the narrow range for high conductivity micro-crystalline films, a more systematic set of experiments is planned in order to grow micro-crystalline a-SiC:H films which have higher bandgap and conductivity.

It is widely reported in the literature that hydrogen dilution improves the electronic properties of the a-SiC:H films by reducing void volume within the films. Based on experiments in our laboratory with a-SiN:H and a limited number of experiments with SiC:H, we expect hydrogen dilution to play a significant role in the corrosion properties of the films as well. During December, we deposited intrinsic a-SiC:H from gas mixtures with the same SiH<sub>4</sub>/CH<sub>4</sub> ratio with no hydrogen dilution, 50% hydrogen dilution and 90% hydrogen dilution. The samples were deposited on 7059 glass, Si wafers, and molybdenum substrates to allow optical, electronic and corrosion properties in alkaline and acid solution to be measured.

Although no significant external leaks were found in the plasma deposition system after replacement of the turbopump, we continued to see a peak at AMU 28 on the residual gas analyzer prior to deposition which was cause for concern. A more thorough helium leak check turned up a minor leak at the exhaust control valve of the turbopump and through the gate valve between the load-lock and deposition chamber. The leak at the exhaust valve has been fixed. The leak from the load-lock is due to an aging rubber gasket. At present, the leaks are minor and the system is maintaining a base vacuum of  $1 \times 10^{-7}$  torr. As a precaution, the load lock chamber is always backfilled with high purity argon and then kept at low vacuum.

Modeling of multijunction photoelectrode behavior has also continued. The student participating in this effort graduates in January. A replacement is being brought onboard the 1st of January to insure a smooth transition. While much of the effort has focused on more accurately describing the solid-state part of the photoelectrode, our attention will now turn to integrating the solid-state model with the physical and electrochemical models developed during an earlier phase of the program. Our near-term goal is to identify catalyst and cell structures which will allow use of tandem amorphous silicon structures with a resultant increase in solar-to-hydrogen efficiency compared to the triple junction devices. We have also made substantial progress in developing our Windows version of the model which will allow easier access and use by others in the photoelectrochemical or photovoltaic fields.

### **Subtask C. Photobiological Production - O. Zaborsky**

Contact was continued with key Japanese researchers and administrators during December to strengthen ties between Hawaii and Japan and to learn more about experimental procedures used by the late Dr. Mitsui and his former students (some now leading researchers in Japan) as well as new protocols now in use at the Marine Biotechnology Institute (MBI).

Dr. Kathleen K. Baker visited (from December 2 through December 13, 1995) the laboratories of Dr. Jun Miyake, Chief Researcher, Molecular Construction Team (Ministry of International Trade and Industry), Tsukuba; Professor S. Miyachi, Executive Managing Director for Research (Marine Biotechnology Institute), Tokyo; Dr. S. Otsuka, Deputy General Manager (Project for Biological Production of Hydrogen), Tokyo; Dr. H. Ikemoto, Chief Scientist (Marine Biotechnology Institute), Kamaishi; and Professor T. Matsunaga, Department of Biotechnology, Tokyo University of Agriculture and Technology (TUAT). This was a follow-on visit to Dr. Oskar R. Zaborsky's visit in November and focused on actual experimental procedures and protocols. The Japanese researchers very kindly gave tours and access to their facilities. Dr. Baker also presented information on the International Marine Biotechnology Culture Collection (IMBCC) in Hawaii at MBI in Kamaishi and TUAT.

At Dr. Miyake's laboratory, the focus of attention was on his *Rhodobacter* (*Rhodopseudomonas*) *sphaeroides*, the strain to be used by Hawaii as the comparison strain. Dr. Miyake desired to have Dr. Baker accept the strain during her visit but that was impossible since regulatory approval first needs to be obtained from Hawaiian authorities. Approval to import this strain has now been initiated. Demonstrations of experimental protocols and equipment needed for the biological measurement of hydrogen production were reviewed with key laboratory personnel so that Hawaii can perform the required evaluations of the Mitsui strains. Pertinent discussions were also held with Dr. Yasuo Asada (also at Tsukuba). Other areas of collaboration included information exchange on the collection, maintenance and documentation of strains (Dr. Miyake, Dr. Miyachi, Dr. Ikemoto and Dr. Matsunaga). All laboratories provided information on their available equipment and sources/manufacturers. At MBI, Dr. Ikemoto presented background information on Dr. Mitsui's strains gathered at the University of Miami (since he was with Mitsui for more than 4 years). Also, protocols and equipment used with the MBI Culture Collection were obtained (e.g., ultra-low freezing techniques, microscope video and differential interference capabilities, and computer databases). At Professor Matsunaga's laboratory, culture procedures were also discussed as well as research interests.

Dr. Matsunaga also visited Hawaii in December and discussions were held on potential research projects with him and Dr. John Benemann, DOE consultant. Follow-up actions may include the preparation of a new RITE project. On administrative matters, several issues dealing with the contract between the University of Hawaii (UH) and RITE are still being resolved. Issues in question pertain to technical details (e.g., the exact nature of the substrates to be tested) and financial policy (e.g., schedule of compensation). Resolution of these issues involves

UH (HNEI), RITE and NEDO administrators. Dr. Sode from TUAT continued his visit and work with the IMBCC culture collection. He submitted a report summarizing his activities on organizing and documenting growth in the cyanobacterial cultures. Also, he presented a seminar on research being conducted in his laboratory in Japan. In addition, Dr. Noriyuki Nakamura and Mr. Akiyo Yamada from Professor Matsunaga's laboratory also worked on the IMBCC collection, specifically on the purple nonsulfur bacteria. They checked the presence of growth in the three replicates of the strains of purple nonsulfur bacteria, prepared a modified RCVB media, and transferred all strains that had obvious growth. Visits and actual work by Japanese scientists at the Bioresources Laboratory (BL) has been extremely active and has been most beneficial to both sides. Dr. Dulal Borthakur previously cloned a fragment of the hupB gene of *Anabaena* sp. PCC7120. Recently, he made a genomic library of this strain in a Lambda cloning vector. He is currently screening the library using the cloned hupB fragment as the probe. Dr. Borthakur has obtained a few positive clones but they need further testing. These will be tested in Southern hybridization. He will continue to screen the clone library until he gets a positive clone that contains the entire hupB sequence. When he gets the entire sequence, he will be able to use the hupB containing fragment as a probe to screen other cyanobacterial strains.

Protocols for use of instrumentation at BL were also developed (e.g., methodology with the Zeiss Compound Axioscope Microscope and Spotmatic Camera). Also, two laboratory assistants started working part-time at BL to provide assistance to Dr. Baker's efforts with the IMBCC.