

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

for

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Project Research: 03163
PR Number 98PR05559-00

ONR POC: Dr. Richard Carlin, ONR-331 (703) 696-5075

Competitive Technology Assistance Program (CTAP)
"Semi-Fuel Cell Power System S&T"

by

Naval Undersea Warfare Center (NUWC)- Newport Division
Code 8231- Propulsion Branch
Newport, RI 02841

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7 July 1998

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PART I

OFFICE OF NAVAL RESEARCH PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 98-PR-05559-00

Contract/Grant Number: N00014-98-AF-00002

Contract/Grant Title: Semi-Fuel Cell Power System S&T

Principal Investigator(s): Christopher Egan

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http address:

- a. Number of papers submitted to refereed journals, but not published: 1
- b. Number of papers published in refereed journals (for each, provide a complete citation): 1
- c. Number of books or chapters submitted, but not yet published: 0
- d. Number of books or chapters published (for each, provide a complete citation): 0
- e. Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
- f. Number of patents filed: 1
- g. Number of patents granted (for each, provide a complete citation): 0
- h. Number of invited presentations (for each, provide a complete citation):
 2
- i. Number of submitted presentations (for each, provide a complete citation):
 2
- j. Honors/Awards/Prizes for contract/grant employees (list attached): 0
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: 0
 Graduate Students: 0
 Post-Doctoral Associates: 0
 including the number of,
 Female Graduate Students: 0
 Female Post-Doctoral Associates: 0
 the number of
 Minority* Graduate Students: 0
 Minority* Post-Doctoral Associates: 0
 and, the number of
 Asian Graduate Students: 0
 Asian Post-Doctoral Associates: 0
- l. Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

a. Abstracts Submitted:

An abstract entitled "Electrode Surface Modification for Cathode Catalysis in Semi Fuel Cells" by R.R. Bessette, J.M. Cichon and D.W. Dischert has been submitted for review, acceptance and subsequent presentation at the Electrochemical Society (ECS) Meeting to be held in Boston, MA, November, 1998. A subsequent paper is planned for publication in the Journal of the Electrochemical Society.

b. Published Papers:

Published Abstract: Aspects of this work and preliminary results were presented by Eric G. Dow and Maria G. Medeiros at the 193rd Electrochemical Society Meeting held in San Diego on May 3-8, 1998, entitled "Solution Phase Catholyte Semi Fuel Cell Utilizing a Flowing Aqueous Electrolyte".

f. Patents Filed:

M.G. Medeiros, S.P. Tucker, R.R. Bessette, J. M. Cichon, D. W. Dischert, "Magnesium-Solution Phase Catholyte Seawater Electrochemical System" Navy Patent Case #78609, submitted June, 1997.

h. Invited Papers:

Aspects of this work and preliminary results were presented by Eric G. Dow and Maria G. Medeiros at the AFOSR/ONR 6.1 Electrochemistry Science and Technology Program Review, 15-16 January, 1998, Ventura, CA. entitled "Solution Phase Semi-Fuel Cells".

Aspects of this work and preliminary results were presented by R.R. Bessette at the AFOSR/ONR 6.1 Electrochemistry Science and Technology Program Review, 15-16 January, 1998, Ventura, CA, entitled "Electrode Surface Modification for Cathode Catalysis in Semi Fuel Cells". Co-authors include J.M. Cichon and D.W. Dischert.

i. Submitted Presentations:

Naval Undersea Warfare Center (NUWC) Division Newport - FY98
Independent Research (IR), PI: Maria G. Medeiros, AI: E. Dow "Magnesium - Solution Phase Catholyte Seawater Electrochemical System". July, 1997.

Naval Undersea Warfare Center (NUWC) Division Newport - FY98
Independent Research (IR), PI: Eric G. Dow, AI(s): R. Bessette and J. Cichon "Surface Stabilization and Characterization of Electrochemical Catalysts for Use in the Aluminum Hydrogen Peroxide Semi-Fuel Cell Battery System". July, 1997.

l. Other Funding:

1) Naval Undersea Warfare Center (NUWC) Division Newport - FY98
Independent Research (IR), "Magnesium - Solution Phase Catholyte Seawater Electrochemical System", \$60K, FY98.

2) Naval Undersea Warfare Center (NUWC) Division Newport - FY98
Independent Research (IR), "Surface Stabilization and Characterization of Electrochemical Catalysts for Use in the Aluminum Hydrogen Peroxide Semi-Fuel Cell Battery System", \$30K, FY98.

3) ONR Grant to University of Massachusetts-Dartmouth, \$25K, 1 Jan 98-30 Sept 98. PI: Russell R. Bessette.

4) Laboratory Participation Program(LPP) from NUWC-Newport Division, \$20K, FY98.

PART II

- a. **Principal Investigator(s):** Christopher Egan
Eric G. Dow and Maria G. Medeiros
- b. **Telephone Number:** (401) 832-2739
- c. **ONR Program Officer:** Dr. R. Carlin, ONR-331
6.1 Electrochemical Science and Technology Program

d. **Program Objectives:**

- 1) Demonstrate 20% improvement in the catholyte polarization potential and electrochemical efficiency via improved catalysis of the cathode.
- 2) Investigate a Magnesium-Hypochlorite (Mg-ClO^-) system in seawater at 10-40 mA/cm^2 ranges to enable up to 600 Wh/kg.

e. **Results To Date:**

Catalysis Results: Nickel substrates catalyzed with Pd and Ir have shown an inability to maintain the catalytic surface. However, planar carbon substrates catalyzed with Pd and Ir and silver foil have shown continued catalytic activity and stable electrochemical performance. Catalyzed carbon yielded the best cell voltage (1.37V) at 250 mA/cm^2 .

Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM/EDS) analysis of Pd and Ir on the substrates show non-uniform coverage of the nickel substrate and uniform coverage of the carbon substrate. X-Ray Photoelectron Spectroscopy (XPS) analyses have also been performed and show that on the carbon substrate very little chloride (Cl^-) is present. Both Pd and Ir exist in a single oxidation state.

Anodic and cathodic efficiency studies using 6.45 cm^2 electrodes in a flow through cell with a 100 mL electrolyte reservoir have been carried out. Initial results show an increase in the aluminum efficiency from 56% with the silver foil to 64% with the combination of Pd/Ir on carbon. In addition, the hydrogen peroxide efficiency increased from 32% to 38% upon replacing silver foil with the combination Pd/Ir on carbon. Other tests utilizing a 100 mL electrolyte reservoir in combination with a 63 cm^2 electrode have yielded H_2O_2 efficiencies in the 60 to 70% range.

Magnesium-SFC Results: Polarization profiles for the Mg-ClO^- system have been performed at room temperature (RT) and at 50°C in a seawater electrolyte in conjunction with 0.7M sodium hypochlorite catholyte. Electrocatalysts of nickel foil catalyzed with palladium and planar carbon catalyzed with palladium and iridium have been tested under the above conditions. The polarizations profiles were performed from 0 to 30 mA/cm^2 and corresponding cell voltages ranging from 1.8V to 1.2V were observed.

Tests at an applied constant current density of 25 mA/cm^2 were also performed for 30 to 60 minute durations. A voltage-time profile reasonably steady at 1.3V was observed when a magnesium anode and an electrocatalyst of nickel foil catalyzed with palladium was tested; however, when a magnesium anode was tested with an electrocatalyst of planar carbon catalyzed with palladium and iridium, the corresponding voltage was steady at 1.5V.

f. Future Plans

Catalysis:

Continue with the SEM/EDS and XPS analyses and include X-Ray Diffraction Spectroscopy (XRD) to identify the chemical composition of the catalyzed species on the substrates.

Quantification of the electrochemical equations that define the decomposition of H_2O_2 and aluminum corrosion reactions will be performed using capillary gas chromatography (GC). GC will be used to measure the hydrogen gas evolved during H_2O_2 decomposition and oxygen gas evolved during aluminum corrosion. Once these gases have been quantified the direct reaction of the aluminum with hydrogen peroxide can be optimized.

Future experiments will also address the low rate performance of the catholyte reduction of hydrogen peroxide and hypochlorite. In addition, the stability of the electrocatalyst as a function of temperature, flow rate, surface composition, substrate preparation and catholyte concentration will be determined.

Magnesium-SFC:

Continue with the optimization of the magnesium-hypochlorite ($Mg-ClO^-$) system; the parameters requiring optimization include catholyte concentration, temperature, flow rate and current density. All testing will be performed on the 1 1/2"X8" (63 cm² electrode area) flowing electrolyte apparatus employing a seawater electrolyte.

Identify and characterize the magnesium electrode surface after testing. Analyses will be performed by Scanning Electron Microscopy in conjunction with Energy Dispersive Spectrometry (SEM/EDS) and X-Ray Diffraction Spectroscopy (XRD). This analysis is critical in solving and eliminating the magnesium hydroxide and magnesium carbonate precipitation problems.

Experiments will also be conducted to evaluate hypochlorite compounds other than sodium hypochlorite ($NaClO$). These commercially available compounds include lithium ($LiClO$) and calcium hypochlorite ($Ca(ClO)_2$). These compounds are available in concentrations greater than 13% which is the maximum concentration achievable for $NaClO$. Testing would be performed on a half-cell (0.5cm² size) utilizing an EG&G Electrochemical system (Potentiostat / Galvanostat).

“Semi-Fuel Cell Power Sytem S&T”

NUWC-NPTDIV / Egan, Dow, Medeiros

UMASS-Dartmouth / Bessette, Cichon

Technology Issues: Development of affordable, long endurance semi-fuel electric propulsion systems to meet the demands of the current and future UUV applications.

Objectives:

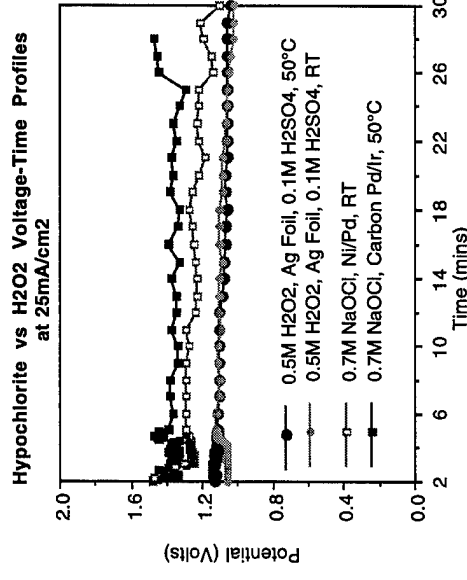
- 1) Demonstrate 20% improvement in the catholyte polarization potential and electrochemical efficiency via improved catalysis of the cathode.
- 2) Investigate a Magnesium-Hypochlorite (Mg-ClO₂) system in seawater to enable up to 600 Wh/kg.

Approach:

- Determine best method of forming a stable and reproducible Pd/Ir catalytic surface
- Perform analyses to identify the chemical composition of the catalyzed species on substrates
- Optimize Mg-ClO₂ system parameters (concentration, flow rate, temp, current density)
- Evaluate LiClO₂ and Ca(ClO₂)₂

Accomplishments:

- Pd/Ir catalyzed carbon substrate yielded best cell voltage, best power, and continued catalytic activity
- SEM/EDS data of Pd/Ir catalyzed on Ni is non-uniform and uniform on carbon
- Mg-ClO₂ polarizations showed voltages ranging from 1.8 to 1.2V at 0 to 30 mA/cm² in seawater only electrolytes
- At an applied 25mA/cm², a cell voltage of 1.5V was observed for 60 min test



Impact & Transition:

- Elimination of the sodium hydroxide electrolyte and activation of the Mg anode in seawater will enable an increase in specific energies by 50% over the state of the art (600 Wh/kg, or 6 times AgO-Zn). As a simpler system, increased reliability and reduced cost will be achieved.
- Achievement of a more stable Pd/Ir catalyzed cathode will significantly improve power and catholyte electrochemical efficiency.

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Figure 1 - Polarization Curves for Catalyzed and Uncatalyzed Substrates

