

OFFICE OF NAVAL RESEARCH
END-OF-THE-YEAR REPORT

for

Grant Number: N00014-98-1-0278

PR Number 98PR03689-00

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

**“Electrode Surface Modification for Cathode Catalysis in
Semi-Fuel Cells”**

by

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PART I

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

PR Number: 98-PR-03689-00

Contract/Grant Number: N00014-98-1-0278

Grant Title: "Electrode Surface Modification for Cathode Catalysis in Semi-Fuel Cells"

Principal Investigator(s): Russell R. Bessette, Ph.D.

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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): 0
- 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: 0
- g. Number of patents granted (for each, provide a complete citation): 0
- h. Number of invited presentations (for each, provide a complete citation):
1
- i. Number of submitted presentations (for each, provide a complete citation):
1
- 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: 0.4
Graduate Students: 0.4
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.

h. Invited Papers:

Aspects of this work and preliminary results were presented by R.R. Bessette at the AFOSR/ONR 6.1 Electrochemical 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: E. G. Dow, AI(s): R.R. Bessette, J.M. 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) Received 6.1 funding of \$135K for FY98 from ONR-33's Competitive
Technology Assistance Program (CTAP)- "Semi-Fuel Cell Power System
S&T"

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

PART II

- a. **Principal Investigator:** Russell R. Bessette
- b. **Telephone Number:** (508) 999-8587
- c. **ONR Program Officer:** Dr. R. Carlin, ONR-331, 6.1 Electrochemical Science and Technology Program

d. Program Objective(s):

1. Identify the optimum conditions for fabricating a stable electrocatalytic cathode of palladium and iridium that will:
 - a. improve the cathode polarization potential
 - b. diminish the heterogeneous decomposition and direct chemical reactions
 - c. significantly improve (gain of 50%) the overall electrochemical cell efficiency
2. To evaluate the electrochemical performance of the catalyzed cathode
3. To characterize the structure and composition of the catalytic surface

e. Significant Results:

Comparison of the cell voltages measured at 250mA/cm² for a baseline silver catalyst and for planar nickel, reticulated nickel and planar carbon substrates catalyzed with palladium and iridium show the catalyzed planar carbon yields the best cell voltage (1.37V vs. 1.25V for reticulated Ni) and thus the best power. Multiple discharges at 100mA/cm² for 45 minutes followed by the acquisition of a polarization curve show continued catalytic activity and stable electrochemical performance for catalyzed carbon and silver foil substrates only. The catalyzed carbon electrode exhibits the highest cell voltage between 50 and 300 mA/cm².

Scanning Electron Microscopy (SEM) data of Pd and Ir catalyzed nickel and planar carbon substrates show non-uniform coverage of the nickel substrate but uniform coverage of the carbon substrate. Energy Dispersive Spectrometry (EDS) analysis of the surface confirms the SEM results.

X-Ray Photoelectron Spectroscopy (XPS) spectra of Pd alone, Ir alone and the Pd/Ir combination on nickel foil and carbon substrates have been obtained for samples prior to use in an Al-H₂O₂ electrochemical cell. The data to date are very inconclusive. The presence of adventitious carbon and perhaps oxygen make interpretation of the spectra very difficult at this time. Additional experimentation is required. An X-Ray Diffraction (XRD) analysis of the Pd/Ir combination on a nickel substrate suggests the very interesting possibility of the formation of a Pd/Ir solid solution. Again, additional experimentation is needed.

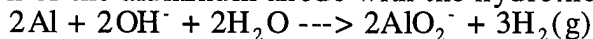
Anodic and cathodic efficiency studies using silver foil and Pd/Ir on carbon as catalysts and EB50V aluminum alloy as the anode show an increase in the Al efficiency from 56% with silver foil to 64% with Pd/Ir on carbon. The H₂O₂ efficiency increases from 32% with silver foil to 38% with Pd/Ir on carbon. The overall low efficiency numbers for the H₂O₂ reduction is believed to be due to the small electrode area (6.45 cm²) used relative to the 100 mL electrode reservoir.

Other tests utilizing a 100 mL electrolyte reservoir in combination with a 63 cm² electrode have yielded H₂O₂ reduction efficiencies in the 60 to 70% range. Additional efficiency determinations using the larger electrode surface area while keeping the electrolyte volume at 100 mL are planned.

f. Summary of Experimentation Plan

X-Ray Photoelectron Spectroscopy (XPS) and SEM/EDS analyses will continue to be used with addition of X-Ray Diffraction Spectroscopy (XRD) to characterize the structure of the catalyzed surface. Initial elemental distribution data have been obtained by XPS. Ultimately the chemical composition of the species on the surface needs to be determined.

Capillary gas chromatography (GC) will be used for evolved oxygen and hydrogen gas analyses. The $O_2(g)$ analysis will quantify the H_2O_2 decomposition process. The $H_2(g)$ analysis will quantify the corrosion reaction of the aluminum anode with the hydroxide:



Quantification of the H_2O_2 decomposition and the aluminum corrosion reactions will allow us to quantify the direct reaction of the Al with the H_2O_2 . We will then be able to perform experiments to minimize this direct reaction.

Once a stable catalytic deposit is achieved, uniform catalysis of nanosized (extremely high surface area per unit volume upwards of $10,000 \text{ cm}^2/\text{cm}^3$) material of either carbon or nickel will be attempted. Successful completion of these experiments should lead to very high (>85%) efficiency for the reduction of H_2O_2 catholyte or the newly proposed hypochlorite (ClO^-) catholyte.

Experiments will be designed to quantify the low rate performance of the catholyte reduction (H_2O_2 and ClO^-) and stability of the electrocatalysts as a function of temperature, flow rate, surface composition, substrate preparation and catholyte concentration.

Characterization of the fundamental chemical and electrochemical equations that describe these phenomena occurring at the electrode surfaces will be accomplished.

g. Students Working on the Project

Mr. James M. Cichon, MS Chemistry candidate at UMASS-Dartmouth, began a position at Duracell, Inc. in Needham, MA on 29 June 1998. He will also be involved in the completion of his work on this project over the next 3 to 6 months.

Mr. Craig Deschenes, BS Chemistry candidate at UMASS-Dartmouth, began work on this project on 15 June 1998. He will work 24 hours per week throughout the summer and will continue to be actively involved with this project during academic year '98-'99.

Electrode Surface Modification for Cathode Catalysis

in Semi-Fuel Cells

Bessette/Cichon, UMASS-Dartmouth

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

Objectives: To identify the optimum conditions for fabricating a stable electrocatalytic cathode of palladium and iridium; to improve the cathode polarization potential; to diminish the heterogeneous decomposition and direct chemical reactions; to significantly improve (gain 50% relative) the overall electrochemical cell efficiency

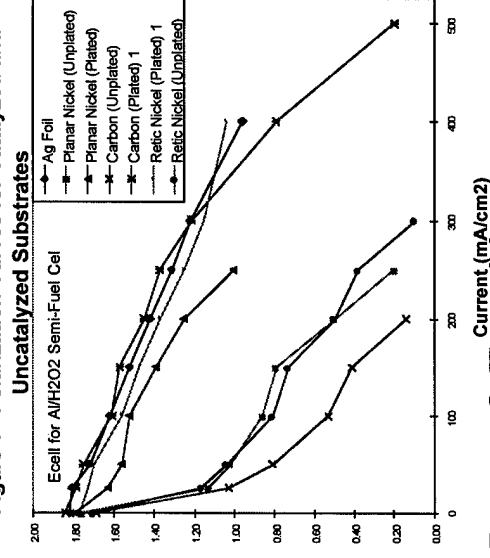
Approach:

- Utilize SEM/EDS and XRD to characterize the structure of the catalyzed surface
- Perform GC analyses of evolved gases (O_2 and H_2) to quantify H_2O_2 decomposition and Al reactions (corrosion/direct)
- Determine best method of forming a stable and reproducibly performing Pd/Ir catalytic surface
- Quantify electrochemical efficiencies

Accomplishments:

- Pd/Ir catalyzed carbon substrate yielded best cell voltage, best power, continued catalytic activity and stable electrochemical performance
- SEM and EDS data of Pd/Ir catalyzed on Ni is non-uniform and uniform on carbon
- Al oxidation and H_2O_2 reduction efficiencies increase for Pd/Ir catalyzed carbon vs. Ag foil catalyst

Figure 1 - Polarization Curves for Catalyzed and



Impact & Transition:

- Developments on a solution phase catholyte for Al aqueous batteries at reduced current densities indicate specific energies in excess of 200 Wh/lb are possible utilizing sodium hydroxide mixed with seawater as caustic electrolyte
- Achievement of a more stable Pd/Ir catalyzed cathode will significantly improve power and catholyte electrochemical efficiency and allow application in a hypochlorite catholyte system

Electrode Surface Modification for Cathode Catalysis in Semi-Fuel Cells

Bessette/Cichon, UMASS-Dartmouth

Table 1:
Catalytic Performance For
Successive Runs After Cell Discharge
at 100 mA/cm² for 45 Minutes Between Runs

Run #	Planar Carbon (V)*	Retificated Nickel (100 ppi) (V)*
1	1.37	1.25
2	1.46	1.26
3	1.34	1.20
4	1.48	1.11
5	1.33	1.06
6	1.38	1.00
7	1.29	
8	1.20	
9	1.35	
10	1.27	
11	1.21	
12	1.00	

* Ecell at 250 mA/cm² for Al/H₂O₂ Semi-Fuel Cell

Figure 2 - Polarization Curves for Catalyzed Substrates After 3.75 hours

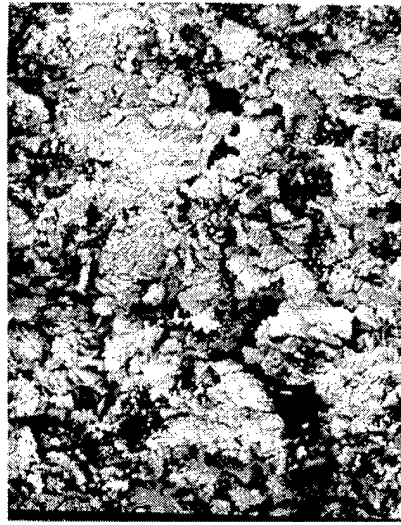
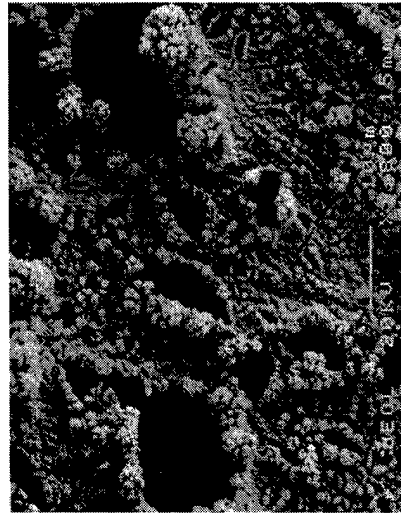
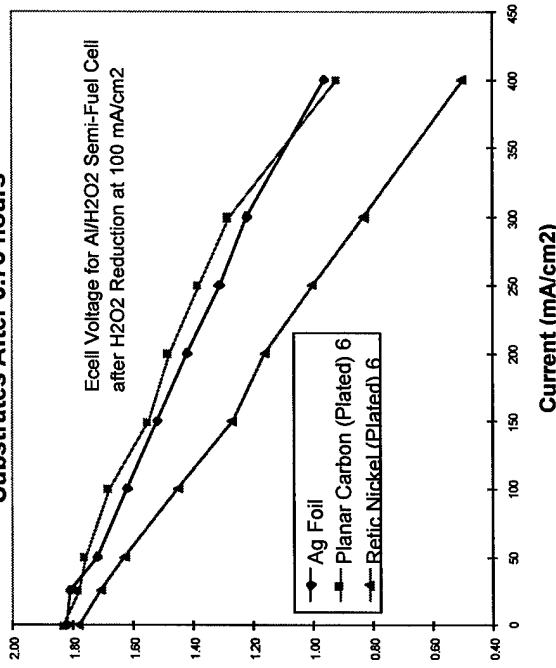


Fig. 3 - Pd/Ir on Planar Nickel Topography Fig. 4 - Pd/Ir on Planar Carbon Topography