The Development of a Magnesium-Hydrogen Peroxide Semi-Fuel Cell

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***Abstract* - The Naval Undersea Warfare Center (NUWC) Division Newport, Rhode Island is presently developing a Magnesium-Solution Phase Catholyte Semi-Fuel Cell (Mg-SFC) as an energetic electrochemical system for low rate, long endurance unmanned undersea vehicle (UUV) applications. This novel electrochemical couple consists of a magnesium anode and a solution phase catholyte of hydrogen peroxide together with a seawater electrolyte.**

Critical to this effort was the successful development of a unique catalytic compound consisting of palladium and iridium together with a carbon based substrate, greatly enhancing the electrochemical reduction of hydrogen peroxide. An overall cell potential increase of +0.9 V (1.25 V to 2.12 V) was observed with this catalyst in place of the prior silver based catalyst; representing a 69.6 % increase in cell voltage.

To further enhance the reduction potential at the positive electrode and the subsequent increased specific energy of this system, NUWC has collaborated with The University of Massachusetts to develop and synthesize a novel high surface area per unit volume Microfiber Carbon Electrode (MCE) using a textile science flocking technique. Use of the flocking technique, which involves the alignment and placement of highly conductive and high surface charge carbon microfibers via a high potential electric field (40 kV to 70 kV), has not been reported upon in the scientific literature. Volumetric surface area of 182 cm^2/cm^3 has been achieved, and the resulting electrochemical payoffs will be discussed.

I. INTRODUCTION

Development of affordable, safe, highly energetic and long endurance technology to meet the demands of current and future unmanned underwater vehicle propulsion systems is a major technical challenge. The magnesium based electrochemical couples [1] have theoretical cell potentials higher than that of the present state of the art seawater activated electrochemical couples for undersea electric propulsion systems [2], with the added advantages that they are light in weight, environmentally friendly and not overly expensive. These solution phase systems are very capable of performing as high energy density sources for low power and long endurance UUV applications.

The redox potentials versus SHE associated with the magnesium-hydrogen peroxide (Mg-H_2O_2) [3,4] system are:

Anode: $Mg \rightarrow Mg^{2+} + 2e^-$ 2.38 V (1)

Cathode: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ 1.77 V (2)

Cell: $Mg + H_2O_2 + 2H^+ \rightarrow Mg^{2+} + 2H_2O$ 4.14 V (3)

Unfortunately these theoretical open circuit potentials are reduced and the electrochemical performance inhibited by the following parasitic reactions:

Decomposition Reaction:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow \quad (4)$$

Direct Reaction:

$$Mg + H_2O_2 + 2H^+ \rightarrow Mg^{2+} + 2H_2O \quad (5)$$

Precipitation Reactions:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \ (s) \quad (6)$$

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3 \ (s) \quad (7)$$

The precipitation reaction produces solid magnesium hydroxide and magnesium carbonate. The magnesium hydroxide results from the interaction of the magnesium cation with the hydroxyl group produced during the reduction of the catholyte, whereas the magnesium carbonate is a result of the magnesium interacting with the carbonates in seawater.

The objective of this project is the development of an electrochemical couple utilizing a magnesium anode together with a solution phase catholyte of hydrogen peroxide (H_2O_2) [5]. The goals are to ascertain the detrimental effects of the magnesium hydroxide and magnesium carbonate precipitates with time, eliminate these precipitates with the introduction of acid, and investigate the effect of membranes to prevent the direct reaction of the catholyte with the magnesium anode.

This investigation has also centered on achieving very large cathode surface area to volume ratios. Achievement of

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small volume, large surface area cells will permit operation at low H_2O_2 levels further enabling the reduction in size of the H_2O_2 storage tank along with increasing the electrochemical reaction efficiencies by virtue of the decrease in the H_2O_2 decomposition.

II. Experimental Section

Chemicals used included sea salt (ASTM-D 1141-52, Lake Products), hydrogen peroxide (50% CG, Elf Atochem.), sulfuric acid (ACS grade, 96%, Aldrich Chemicals), hydrochloric acid (ACS grade, 36%, Fisher Scientific), phosphoric acid (ACS grade, 85%, Fisher Scientific) and acetic acid (ACS grade, 100%, Fisher Scientific). The 10μm diameter carbon fibers were accurately cut to 0.50 mm in length by Engineered Fibers Technology, LLC. The carbon microfibers were applied to the substrate using a Maag Flockmaschinen Model SPG 1000. The conductive carbon epoxy was obtained from Creative Materials Inc. The carbon paper was 0.25 mm thick, Spectracarb type 2050A-1040, available from E-Tek Incorporated.

A Model 273A Potentiostat/Galvanostat (EG&G Princeton Applied Research) was used in a three-electrode configuration for half-cell characterization. A working electrode of magnesium anode (AZ61) for anode studies and a Pd/Ir catalyzed carbon paper electrodes or MCE for cathode investigations. A silver-silver chloride electrode (Ag/AgCl, Fisher Scientific) served as the reference electrode, and the counter electrode was a carbon rod (type L-3089/Grade AGKSP, Bay Carbon, Inc.).

Dual flow testing was also conducted using the Fig. 1 flowing electrolyte apparatus which accommodates both electrolyte and catholyte tanks and flow loops. One tank contained the seawater electrolyte that was pumped to the magnesium anode. The second tank contained seawater, hydrogen peroxide and acid; this catholyte was pumped to the cathode side of the cell. Data were collected using Laboratory Notebook™ and the analysis was performed using Microsoft Excel™.

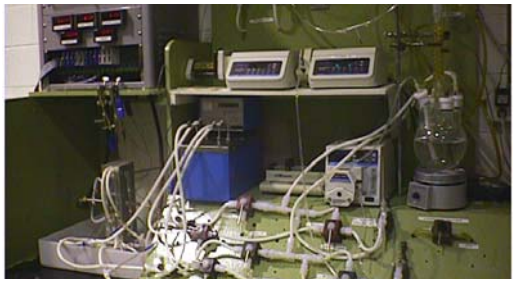

Fig. 1. Mg-H_2O_2 flowing electrolyte apparatus.

The cell fixture is designed to accommodate an ionically conductive inner cell membrane, thus isolating the anode/electrolyte from the catholyte. Two cell fixtures were available, one accommodating electrode sizes of 9.6cm^2 and a second for electrode sizes of 77cm^2.

III. Mg-SFC Investigations

Polarization tests utilizing the flowing electrolyte apparatus shown in Fig. 1 configured with 77 cm^2 electrodes were carried out at 20^oC with a magnesium anode, a silver foil electrocatalyst and a sea salt and hydrogen peroxide electrolyte/catholyte solution. These tests were conducted at current densities ranging from 0 to 50 mA/cm^2.

Using 'seawater-only' electrolyte, i.e. no catholyte, 15 mA/cm^2 was the highest current density achieved with a corresponding voltage of 1.0 V. Higher current densities were not possible due to magnesium precipitates preventing proper electrolyte flow between electrodes.

Experiments incorporating the H_2O_2 catholyte were conducted. As shown in Fig. 2, several acids were investigated in an attempt to solubilize the solid precipitates of magnesium hydroxide ($Mg(OH)_2$) and magnesium carbonate ($MgCO_3$) formed in the Mg-H_2O_2 system. The acids tested included sulfuric (H_2SO_4), hydrochloric (HCl), phosphoric (H_3PO_4) and acetic (CH_3COOH) acids. All tests were performed with 0.1 M concentration of acid and 0.5 M H_2O_2. The best results were achieved with sulfuric acid. The phosphoric acid tests demonstrated higher open circuit voltages (OCV's), however, the polarization profiles exhibited undesirable polarization in the range of 0 to 30 mA/cm^2. A decline in cell polarization was observed when using sulfuric acid, however, the voltages were steady as the current density ranged from 10 to 30 mA/cm^2.

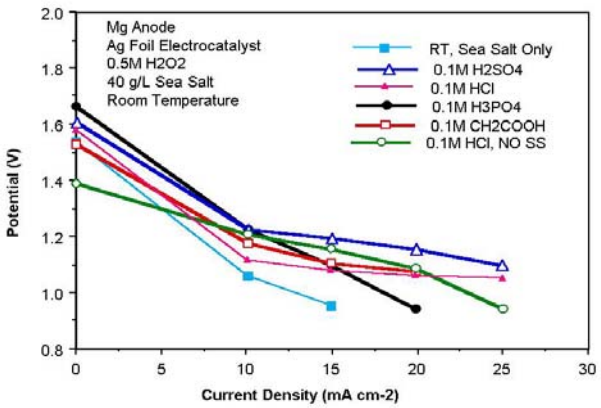

Fig. 2. Polarization profiles for magnesium anodes with hydrogen peroxide at room temperature.

Half-cell polarization experiments showed that higher cathodic voltages can be achieved when a palladium/iridium

(Pd/Ir) catalyzed carbon paper cathode is substituted for silver foil. The silver foil previously used demonstrates cathodic potentials of -0.4 V vs. Ag/AgCl at a current density of 25 mA/cm^2. However, when the Pd/Ir on carbon paper is used under the same conditions the cathodic voltage is increased to +0.4 V vs. Ag/AgCl. An increase of 800 mV on a cell basis is expected as a result of the Pd/Ir carbon electrode in the acid/seawater/H_2O_2 catholyte electrolyte.

Fig. 3 shows constant current discharge profiles at 25 mA/cm^2 for a Mg-SFC with Pd/Ir carbon paper and Ag foil cathodes. The mean voltage for the Mg-Pd:Ir carbon cell is 2.12 V vs. 1.25 V for the Mg-Ag foil cell. This is an increase of 70% in voltage as a result of the Pd:Ir catalyzed carbon in place of Ag foil. The efficiencies calculated for these tests ranged from 5 to 20% for both the Mg and the H_2O_2. The low efficiencies were due to the direct reaction of the hydrogen peroxide/acid catholyte with the magnesium anode. To reduce this direct reaction of the catholyte with the anode, a membrane was introduced between the anode and cathode compartments. The membranes tested included Viskase Corporation SF296, RD65 (3.5 mils), NAL870, and NAG676; from Celgard Corporation 2300 and 5500; from Dupont Nafion 112 and 115 and from UCB Films 350POO. The best results were observed with membranes Nafion 112 and 115, and Viskase SF296.

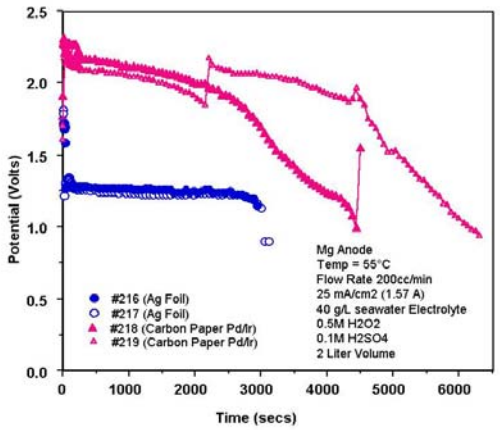

Fig. 3. Constant Current Profiles for Mg-SFC

Fig. 4 shows a discharge profile at 25 mA/cm^2 when a Nafion 115 membrane was used. The anode was Mg (AZ61), the cathode was carbon paper catalyzed with Pd/Ir (1:1 ratio). The electrolyte for the anode was 40 g/L seawater at 55°C, and the catholyte was 0.5 M H_2O_2, 0.1 M H_2SO_4, and 40 g/L seawater at 55°C. The voltage observed was 1.8 V for the duration of the test and the corresponding Mg efficiency was 85%.

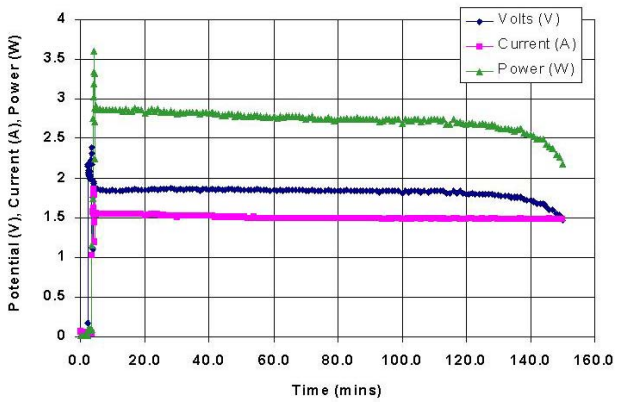

Fig. 4. Voltage, current and power profile for Mg-H_2O_2 utilizing Nafion 115 membrane.

The advantages of the separated flow concept are numerous. First, the direct reaction between the Mg anode and the H_2O_2 catholyte has been decreased significantly. As a result anode efficiencies have improved from the 10 to 20% range, without a membrane, to the 75 to 85% range with a membrane in place.

Following the optimization of the parameters for the Mg-H_2O_2 system [7], several experiments were conducted to determine catalyst stability with time along with the start/restart capabilities. Constant current density discharge experiments were performed in 8-hour intervals. The 8-hour time limit was due to the limited mass of the Mg. After each 8-hour test, the magnesium anode was replaced and the experiment was restarted and continued for another eight hours. This was conducted for five experiments. The last experiment utilized "real" seawater versus the synthetic seawater (Lake Products). No differences in voltage or efficiency were observed over the entirety of this test sequence, nor was there any difference between the "real" seawater experiment and the synthetic seawater experiment.

IV. High Surface Area Catalysis Investigations

The simultaneous deposition of Pd and Ir on the carbon substrate was carried out by cyclic voltammetry from –150 mV to –300 mV vs. Ag/AgCl at a rate of 1.0 mV/s using a EG&G Instruments, Inc. Model 273A potentiostat/galvanostat and associated data acquisition system. The degree of loading was controlled by carrying out the deposition for exactly 25 cycles. The solutions used for the deposition were heated to 70^{O}C and contained 2.0 mM palladium (II) chloride ($PdCl_2$), 2.0 mM sodium hexachloroiridate (IV) (Na_2IrCl_6), 0.2 M KCl, and 0.1 M HCl. The carbon electrode was soaked in 6 M HCl for 15 minutes and rinsed with distilled water prior to use. A three-electrode cell consisting of the carbon substrate working

electrode, a Ag/AgCl reference electrode, and a Pt auxiliary electrode was used for the depositions.

The procedure described above was utilized for the deposition of Pd/Ir onto carbon paper electrodes used in the Mg-SFC investigations described earlier. This same procedure was also used for the deposition of Pd/Ir onto the novel Microfiber Carbon Electrode (MCE) presently under investigation.

High surface area MCE's are being developed to increase cell efficiency and rate performance. These electrodes are prepared using a textile technique called flocking. This technique involves the alignment and distribution of carbon microfibers, nominally 10 μm in diameter and 500 μm long, onto a substrate through the use of a strong electrostatic charge of 40 kV to 70 kV. The substrate is carbon paper coated with a conductive carbon ink. Before the ink is cured, the fibers are accelerated and aligned through the high voltage field and embedded onto the ink. The ink is then cured at 100°C for one hour.

Fig. 5 depicts SEM micrographs of top and cross section images of a MCE. This electrode was fabricated using a 250 µm thick film of conductive ink to bind the fibers to the carbon paper substrate.

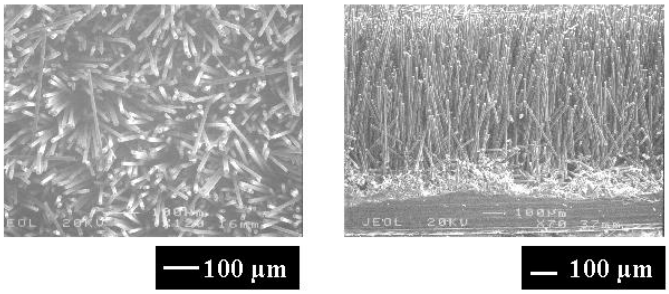

Fig. 5. SEM micrographs of a microfiber carbon electrode
Left: top view; Right: cross section view

The conductive ink used in the fabrication of the MCE is a key component. It must bind the fibers and bind itself effectively to the substrate while not introducing significant potential (IR) loss in the cell. Initial fabrication experiments have shown a carbon conductive ink (Creative Materials, Inc.) to have excellent physical properties for our use. Excellent adhesion of the fibers has been obtained. A Bird type applicator allowed application of a uniform film of the ink on the substrate. A porous carbon paper (0.25 mm thick, Spectracarb) has proven to be an excellent substrate for bonding of the conductive ink. In addition, it remains rigid during electrochemical deposition of the Pd:Ir catalyst at 70°C.

The fiber density of the MCE shown in Fig. 5 was determined to be 55,700 fibers/cm^2 of electrode geometric area, i.e. the two dimensional area defined by the carbon paper. MCEs having 112,000 fibers/cm^2 of geometric area have been prepared. The electrode having the latter fiber density has 182 square centimeters of surface area per cubic centimeter of electrode volume. This electrode volume includes the thickness of the conductive ink binder and the carbon paper substrate.

Application of a Pd/Ir catalyst to carbon microfibers with a 100:1 aspect ratio (1.0 mm L x 0.010 mm D) was non-uniform. The catalyst deposited at the top one third of each fiber. Fairly complete coverage of each fiber by the catalyst was achieved with fibers having 50:1 and 25:1 aspect ratios. Fig. 6 shows top views of the 50:1 aspect ratio fibers (0.5 mm L x 0.010 mm D) of the MCE covered with catalyst for the entire length of the fibers. Well formed palladium and iridium clusters are clearly shown. It is likely that an increase in surface area of several times occurs with the application of the catalyst.

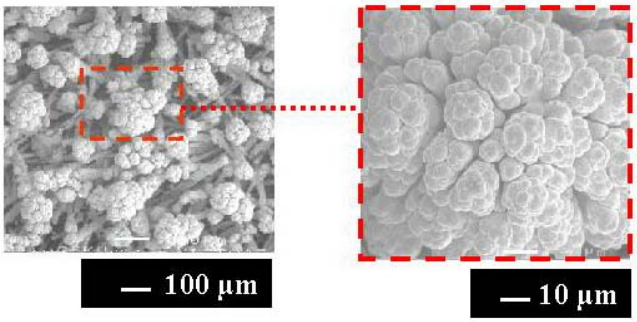

Fig. 6. Scanning electron micrographs of the Pd:Ir catalyzed MCE

Experimental polarization of the MCE electrode was conducted and evaluated against the baseline carbon paper electrode. The results shown in Fig. 7 demonstrate how the MCE electrode enables increased current density while allowing reduced catholyte flow rates; a characteristic which will greatly improve overall system efficiency. Flow rates of 200/100 and 25/12 correspond to anolyte/catholyte flows, respectively, in units of cc/min.

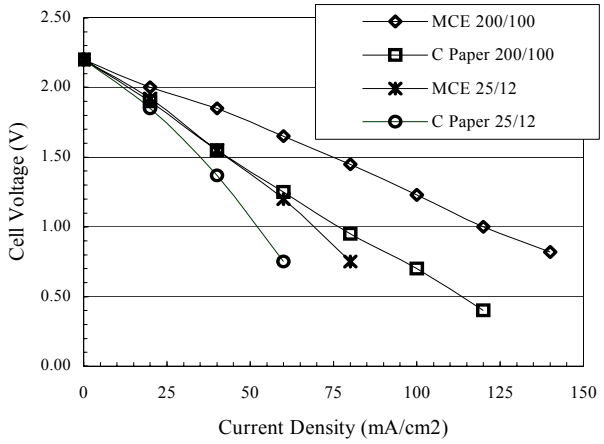

Fig. 7. Cell polarization at 0.25 M H_2O_2 using MCE electrode versus baseline carbon electrode for various anolyte/catholyte flow rates.

Significant to this effort is the realization that the MCE electrode, by virtue of its increased surface area, enables not only reduced cell polarization, but also, enables the use of significantly lower concentrations of catholyte. Fig. 8 displays the cell polarization at a greatly reduced H_2O_2 catholyte concentrations of 0.06 M. Inspection of Figs. 7 and 8 indicates the MCE electrode at 0.06 M catholyte concentration is comparable in voltage to the baseline carbon electrode at 0.25 M catholyte concentration. This reduction in catholyte concentration is significant in that it will greatly reduce catholyte heterogeneous decomposition resulting in increased system efficiency.

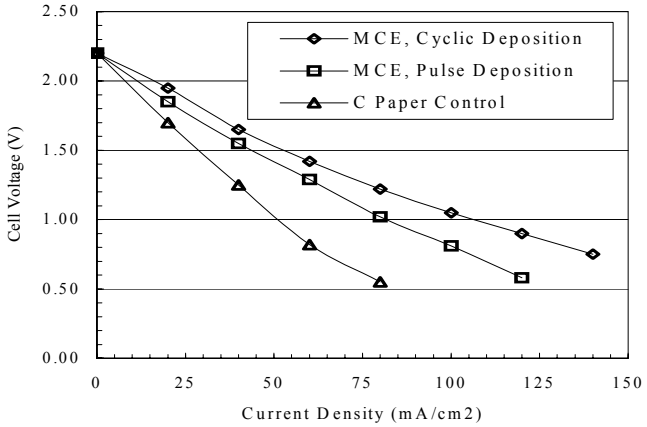

Fig. 8. Cell polarization at 0.06 M H_2O_2 using MCE electrode versus baseline carbon electrode

V. Conclusions

A Magnesium-Solution Phase Catholyte Semi-Fuel Cell (Mg-SFC) system is undergoing investigation as an energetic electrochemical system for low rate, long endurance undersea vehicle applications. This electrochemical system consists of a magnesium anode and a solution phase catholyte of hydrogen peroxide in a seawater electrolyte.

Full-cell testing showed voltages of 1.25 V using Ag foil as the electrocatalyst and 2.12 V when Pd/Ir on carbon paper is substituted; a 70% voltage increase.

A goal to minimize/eliminate the direct reaction between the magnesium anode and the catholyte hydrogen peroxide while maintaining high efficiencies was met with Viskase SF-296 and Nafion NF115 membranes. Anode efficiencies above 80% were achieved when using a membrane. In comparison, anode efficiencies of less than 20% were realized when a membrane is not utilized.

Microfiber Carbon Electrodes (MCEs) of significant fiber density have been fabricated using a textile science flocking technique; a volumetric surface area of 182 cm^2/cm^3 has been achieved. Stable Pd/Ir catalyst cluster formation over most of the carbon fiber surface area has been demonstrated. The Pd/Ir catalyst cluster formation is expected to increase the volumetric surface area several fold.

The MCE electrode demonstrated the ability to operate at greatly reduced concentrations of catholyte, 0.06 M down from 0.25 M, while maintaining cell voltage and increasing efficiency.

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