

REPORT DOCUMENTATION PAGE

*Form Approved
OMB No. 0704-0188*

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 04-05-2005		2. REPORT TYPE Final		3. DATES COVERED (From - To) 15 March 02-30 Sept. 04	
4. TITLE AND SUBTITLE Catalysis, Architecture and the Electrochemical Performance of Microfibrous Cathodes for Hydrogen Peroxide Based Fuel Cells				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER N00014-02-1-0424	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Russell R. Bessette, Ph.D.				5d. PROJECT NUMBER 04PR07198-00	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Massachusetts Dartmouth Department of Chemistry and Biochemistry 285 Old Westport Rd. N. Dartmouth, MA 02747				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Ballston Centre Tower One 800 North Quincy Street Arlington, VA 22217-5660				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release; distribution is unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT A novel cathode morphology has been developed for use in magnesium-hydrogen peroxide semi-fuel cells. A direct electrostatic flocking method is used to prepare the carbon microfiber arrays that are subsequently catalyzed with a Pd/Ir alloy by electrochemical deposition. The microfibers protrude from a current collector like the bristles of a brush. Flocking under different voltage field strengths and in various atmospheres is reported upon. A pulse potential deposition technique is compared to the baseline cyclic potential method. XRD data are presented to conclude that a homogeneous alloy of Pd and Ir is obtained by both techniques. Polarization and constant current results show these electrodes significantly improve the rate capability of the Mg-hydrogen peroxide cell. Individual electrode potential measurements show that most of the polarization occurs on the cathode. Combinations of Co, W and Mo with Pd and Ir have been studied to improve catalytic activity. Bipolar electrode fabrication has been accomplished. Long term performance data of single cells and two cell stacks are presented. Electrode performance modeling was undertaken.					
15. SUBJECT TERMS Architecture of Catalyzed Microfibrous Cathodes; Palladium-Iridium Catalysis; Magnesium Electrochemical Cells; Hydrogen Peroxide Electrochemical Cells; Semi-Fuel Cells					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Unlimited	18. NUMBER OF PAGES 30	19a. NAME OF RESPONSIBLE PERSON Russell R. Bessette, Ph.D.
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 508-999-8587

Office of Naval Research

Final Technical Report

for

Grant Number: N00014-02-1-0424

PR Number: 04PRO7198-00

ONR POC: Dr. Michele Anderson, ONR 331 (703) 6961938

**"Catalysis, Architecture and the Electrochemical
Performance of Microfibrous Cathodes for
Hydrogen Peroxide Based Fuel Cells"**

by

Russell R. Bessette, Ph.D.

**University of Massachusetts Dartmouth
Department of Chemistry and Biochemistry
285 Old Westport Road
North Dartmouth, MA 02747**

December 30, 2004

**Coworkers: Charles J. Patrissi, Maria G. Medeiros, Louis G. Carreiro, Yong K.
Kim, Steven P. Tucker, Craig M. Deschenes, Christopher N. LaFratta, Michelle M.
Dunnell, Delmas W. Atwater, Thomas M. Arruda, Derek P. Gomes**

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

This document has been approved for public release and sale. Its distribution is unlimited.

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

March 15 - September 30, 2002 (FY 02)

Technical Objectives

The objectives of the present investigation are to optimize the flocking process parameters for fabrication of carbon microfiber electrodes, and to study by electrochemical techniques the formation of catalyst Pd/Ir nanoparticles versus other binary/ternary combinations of Pd, Ir, Co, W, Bi, and Mo to improve catalytic activity. An additional objective is to evaluate catalyzed microfiber-HEIP (high electrolyte penetration) electrodes in a magnesium-hydrogen peroxide semi-fuel cell.

Technical Approach

1. Optimization of Flocking Process Parameters for Fabrication of Carbon Microfiber Electrodes

Carbon fiber electrodes were investigated to achieve maximum electrolyte penetration and electrochemical efficiency, while maintaining a minimal H_2O_2 concentration in the cell. Structures which maximize conduction across the cell and which minimize the mass transfer layer thickness at the electrode-electrolyte interface were studied.

A Textile Science flocking technique was used to fabricate the carbon fiber electrodes. A schematic diagram of the flocking process that depicts the various parameters is shown in Figure 1.

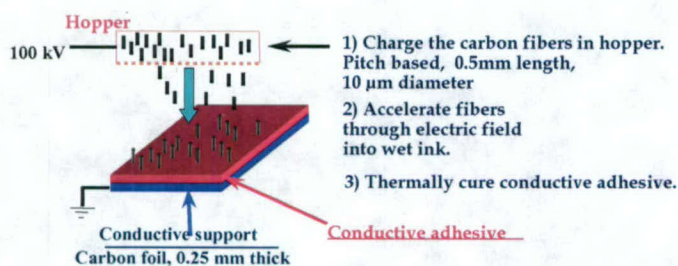


Figure 1: Schematic Diagram of Flocking Process

Parameters studied include the applied field strength, the thickness of the conductive ink layer and the separation of the electrodes in the flocking apparatus. The field strength per cm of distance between the electrodes at a particular thickness of carbon ink layer was studied. Optimization of the ink thickness and viscosity was pursued to provide effective binding of the fibers while minimizing the resistance obtained from the binder layer. Additional experiments were carried out to achieve reproducibility in fiber density in the +/- 5% range and to attain the homogeneity desired in the fabrication of larger electrodes i.e. 1.5" x 8" electrodes and ultimately full scale approx. 14" diameter electrodes. Control of the carbon fiber density to achieve maximum surface area with high electrolyte penetration will be needed to achieve >90% H₂O₂ reduction efficiency with concentrations less than 10mM.

The fabrication of bipolar electrodes, where these high surface area electrodes are constructed on the backside of anodes was investigated. Flexible graphite that has good conductivity and can be shaped was evaluated as the electrode substrate. An additional advantage of this substrate is that it can act as a barrier in the bipolar configuration.

2. Formation of Catalyst Nanoparticles by Electrochemical Techniques

Pulse potential deposition techniques of the electrocatalyst were studied along with cyclic voltammetry. Polarization curves for the reduction of H₂O₂ on the catalyzed surfaces were obtained using an EG&G Model 273A Electrochemical System. Onset potentials, Tafel slopes and exchange current densities were evaluated.

The electrocatalyst most extensively studied has been a palladium-iridium combination. Investigation of ternary metal systems to improve catalytic activity was undertaken. Improved polarization curve exchange current densities for the reduction of H₂O₂ and a shift to a more positive onset potential were used to evaluate the catalytic activity. The ternary systems studied include Co-Pd-Ir, Mo-Pd-Ir, Bi-Pd-Ir and W-Pd-Ir. Surface analysis techniques (SEM, EDS) were utilized to characterize the catalytic surface. The scanning electron microscopy (SEM) was carried out using a JEOL USA Model 6300 instrument. The SEM working distance was 15 mm giving a resolution of 5.0nm.

3. Evaluation of Catalyzed Carbon Microfiber-HEIP Electrode Performance in a Mg-H₂O₂ Semi-Fuel Cell

The fabricated cathodes were tested toward the reduction of H₂O₂ in combination with magnesium anodes and acidic electrolyte in a new 1 x 1.5" flow through apparatus. Cell Voltage-Current profiles and constant current tests at low and high current densities were investigated.

Direct titration of H₂O₂ was used to monitor change in its concentration. Magnesium use was monitored through mass measurements. Finally, quantification of the percent efficiency for all of the reactions was calculated.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS) were used to determine catalyst morphology and elemental composition, respectively. The physical nature of the catalytic surface before and after repeated use in the electrochemical cell was monitored.

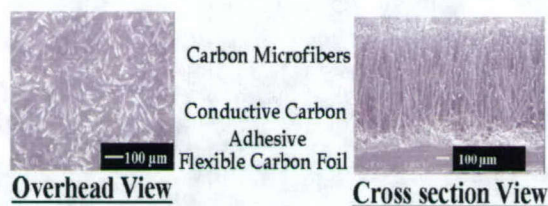
Progress

1. Optimization of Flocking Process Parameters for Fabrication of Carbon Microfiber Electrodes

a. Fabrication

Carbon microfiber arrays were prepared by electrostatic flocking. The carbon microfibers were placed in a hopper at the bottom of which was the negative electrode of the flocking apparatus. The hopper was held vertically above the substrate. The carbon paper or foil substrate with conductive ink was taped to a 4" X 6" aluminum plate and was placed on the opposite electrode held at ground potential. The electrode separation was 10 to 30 cm. Upon application of a 40 to 100kV electric field, the carbon fibers were charged and accelerated through the electric field into the wet ink. The electric field strength was thus varied between 4 and 6 kV/(cm of electrode separation). The flocking time was 10sec to 20sec. After flocking, the conductive adhesive was thermally cured. The fibers of the carbon microfiber array (CMA) shown in figure 2 are 0.5mm in length, the conductive ink is 0.100mm thick and the carbon foil substrate is 0.25mm thick. Thus, the entire array is approximately 0.7mm thick

Figure 2 Scanning Electron Microscopy of Carbon Microfiber Array Prepared By Electrostatic Flocking



Carbon paper (Spectracarb) also 0.25mm thick was used as a control substrate in these studies. This paper is really a bed of carbon fibers and, therefore, does not provide an impervious barrier to a current collector. A 0.100mm thick layer of ink (Creative Materials) was applied to the backside of the paper to provide a barrier to the current collector.

b. Carbon Ink vs. Foil and Barrier Properties

It was found that the carbon ink did not provide a reproducible impervious barrier since it tended to develop small cracks as it cured. Carbon foil (Alfa Aesar, 99.8% C) 0.125mm and 0.250mm in thickness were tested as impervious barriers to the current collector in a

monopolar cell. Electrodes prepared with the thin carbon foil did not have suitable strength. The foil tended to crease or crack with use. Electrodes prepared with the thicker 0.250mm foil could be readily handled without any creasing or cracking occurring.

c. Conductive Ink Layer Thickness Determination

The thickness of the ink was varied between 0.050mm and 0.250mm. The thin ink layer did not reproducibly retain the fibers during the flocking process and the thick layer resulted in fibers laying over and thus not being sufficiently perpendicular to the substrate. A 0.100mm thick layer of ink proved to be optimum for the 0.5mm fibers used.

d. Electric Field Strength Optimization

The electric field strength, defined as kV per centimeter of distance between the electrodes in the flocking apparatus, was also studied. For the 0.100mm thick layer of conductive ink, the optimum field strength was found to be 5 kV/cm. Field strengths between 2.5 and 6 kV/cm were investigated. The optimum field strength was determined by electrode performance in a Mg-H₂O₂ SFC and by scanning electron microscopy studies.

e. Fabrication of a Bipolar Electrode

A bipolar electrode is necessary for the successful deployment of a Mg-H₂O₂ SFC. The electroactive components are a catalyzed cathode for the fast reduction of H₂O₂ and a metal anode such as Mg. The two must be electrically connected and as close as possible while being isolated from the electrolyte of the other to minimize leakage currents and maximize efficiency. That is, the metal anode must not be exposed to the catholyte and the catalyst must be isolated from the anolyte. To accomplish this, the bipolar electrode will contain a graphite foil sheet that will act as an electronically conductive barrier between the metal anode and the catalyst. The graphite foil has high electrical conductivity, it is chemically inert, and it is nonporous. The graphite foil will be coated on both sides with a conductive carbon screen printing ink. The screen printing ink will serve two functions. One will be as a support for the catalyst directly or for carbon fibers that will support the catalyst. Adhesion between the cured ink and a Pd/Ir catalyst has been found to be excellent such that it cannot be physically removed even by rubbing with a wet finger. The opposite side of the graphite foil is coated with a layer of the conductive ink that is used to bond the catalyst/ink/foil or catalyst/fibers/ink/foil composite to the metal anode.

The ink is also a critical enabler for the stability and performance of the bipolar electrode. The adhesive ink must have enough cohesive strength to maintain the integrity of the bipolar composite electrode. In addition, it will be exposed directly to the peroxide/acid/salt water electrolyte so it must be stable in the low pH, oxidizing

environment. Preliminary tests show that, in fact, it is stable over the expected operating life of a UUV mission and has excellent conductivity.

2. Formation of Catalyst Nanoparticles by Electrochemical Techniques

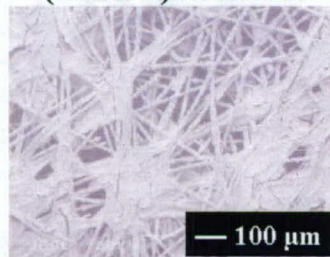
A palladium/iridium catalyzed carbon microfiber array yielding a high electrolyte penetration (HEIP) electrode is shown in Figure 3A. While Pd/Ir nodules are clustered at the tips of the fibers, the SEM image shows the entire length of the fibers to be covered by catalyst. Figure 3B shows a Pd:Ir catalyzed paper (control) electrode. This paper control is seen to be really a mat of carbon fibers. Figure 3C shows the typical Pd:Ir nodules that are obtained upon electrodeposition of these catalyst metals. The diameter of these nodules is in the 3 to 5 μm range.

Figure 3A Pd:Ir Catalyzed Carbon Microfiber Array-HEIP Electrode



Top View

Figure 3B Planar Carbon Paper (Control) Electrode



Pd-Ir Catalyzed

Figure 3C Pd:Ir Nodules on Carbon Paper



Cyclic Voltammetry vs. Pulse Potential Deposition

In an attempt to reduce the time of deposition from the control Pd/Ir deposition conditions, pulse potential deposition at various cycles and delay times were investigated. The control conditions were cyclic voltammetry, -0.15V to -0.30V , 1.0 mV/s for 25 cycles using a solution of 2.0mM PdCl_2 and Na_2IrCl_6 with 0.2M KCl , 0.1M HCl at 70°C . The electrode substrate was 0.25mm thick carbon paper. Evaluative parameters for the control were Pd/Ir ratio of 1:1 as determined by EDS, polarization curve onset potential of 0.627V vs. Ag/AgCl, and a slope of 402mA/V . The linear sweep voltammetry polarization curves were recorded while using 0.5cm^2 electrodes and an electrolyte of $0.25\text{M H}_2\text{O}_2$, $0.2\text{M H}_2\text{SO}_4$, 40g/L NaCl and ambient temperature.

Several pulse potential deposition experiments were carried out using the -0.15V and -0.30V settings with delays of 0.5s and 0.1s at -0.15V and a delay of 0.1s in all cases at -0.30V . The pulse potential cycles were varied from 1,000 to 10,000. In all cases where a 0.1s delay was used at both -0.15V and -0.30V , the onset potentials and polarization curve slopes were considerably lower than the control. The pulse potential deposition carried out for 4000 cycles with a delay of 0.1s at -0.30V and a 0.5s at -0.15V was the only result that showed improvement over the control. In this case a polarization curve slope of 482mA/V was obtained compared to the control value of 402mA/V . The onset potential was slightly lower, however, at 0.619V vs. Ag/AgCl compared to the control value of 0.627V . Longer delay times to allow time for elimination of any mass transport problems at the fiber electrolyte solution interface need to be investigated.

The electrocatalyst most extensively studied has been a palladium-iridium combination. Investigation of ternary metal systems to improve catalytic activity was undertaken. The starting materials used were 2.0mM level solutions of PdCl_2 , Na_2IrCl_6 , $\text{Bi}(\text{NO}_3)_3$, Na_2WO_4 , Na_2MoO_4 or CoCl_2 . The deposition, polarization and evaluative parameters were the same as those used for the Pd/Ir studies comparing the control cyclic voltammetry with the pulse potential deposition. For the pulsed potential studies, a delay of 0.1s at -0.30V , 0.5s at -0.15V , and 4000 cycles were used. A carbon paper substrate was again used in all cases. SEM and EDS were used extensively to evaluate the catalyst morphologies.

EDS analysis shows a moderate incorporation of molybdenum (Mo), Figure 4B and a slight incorporation of tungsten (W), Figure 5B into the ternary catalyst lattice. Very interestingly, the SEM micrographs show a single-phase system for both of these ternary systems, Figures 4A and 5A.

Fig. 4A SEM Micrographs for Mo

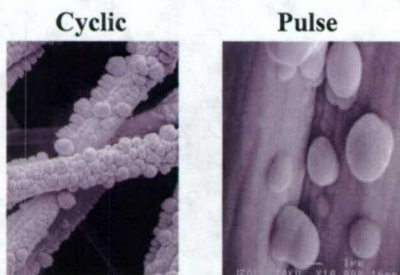


Fig. 4B EDS Spectra for Mo

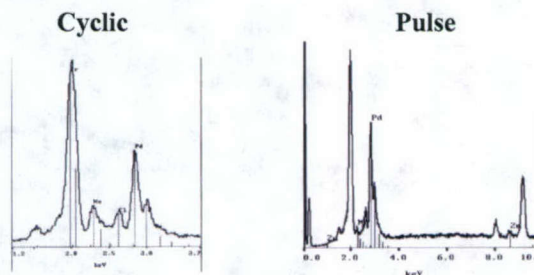


Fig. 5A SEM Micrographs for W
Cyclic Pulse

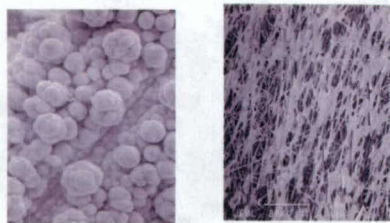
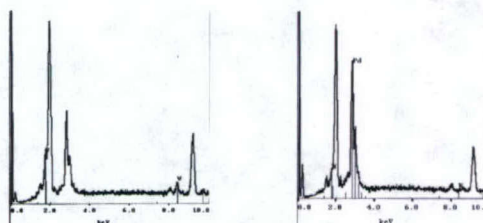


Fig. 5B EDS Spectra for W
Cyclic Pulse



The SEM micrographs show a two-phase catalyst for bismuth (Bi) and the Pd/Ir binary alloy, Figure 6A. The EDS analysis, Figure 6B, is inconclusive since the Bi and Ir lines overlay. The Pd/Ir control SEM micrograph and the EDS spectrum for the alloy prepared by cyclic voltammetry are shown in Figures 7.

Fig. 6A SEM Micrographs for Bi
Cyclic Pulse

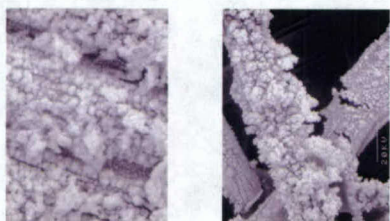


Fig. 6B EDS Spectra for Bi
Cyclic Pulse

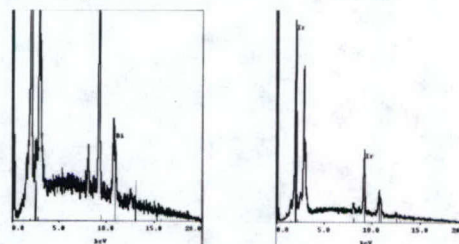
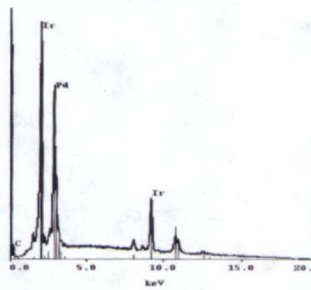
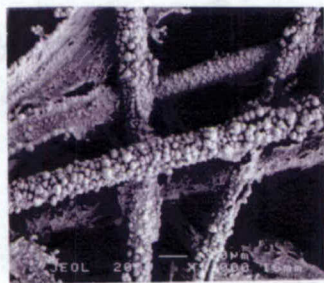


Fig. 7 Pd/Ir Control-Cyclic Voltammetry
SEM Micrograph EDS Spectrum



Cobalt (Co) was not incorporated in the catalyst lattice. No cobalt was found by EDS analysis and in the SEM micrograph.

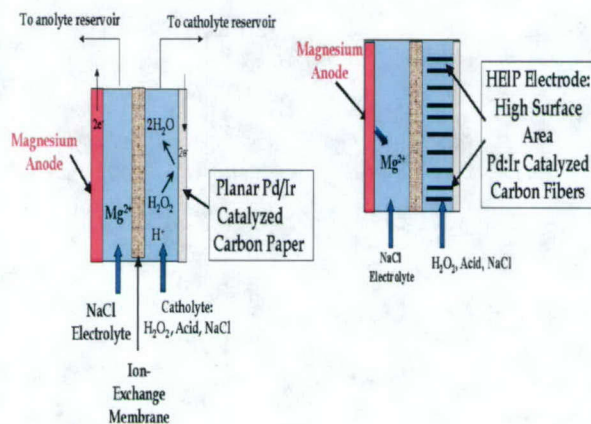
The polarization curve slope was less for the W containing ternary catalyst than the Pd/Ir control for the cyclic voltammetry and the pulse potential depositions. For the Mo ternary catalyst, the polarization curve slope was higher for the catalyst prepared by pulse potential versus the Pd/Ir control (280mA/Vcm^2 vs 236mA/vcm^2) but was not as high when cyclic voltammetry was used (220mA/cm^2 vs 236mA/cm^2). For the Bi ternary catalyst, the polarization curve slope is lower than the control for the catalyst prepared by

cyclic voltammetry and it is essentially the same as the control when pulse potential deposition was used. No significant change in onset potential was obtained for any of the ternary catalysts studied. Further work on the Mo, W and Bi ternary catalysts is warranted.

3. Evaluation of Catalyzed Carbon Microfiber-HEIP Electrode Performance in a Mg-H₂O₂ Semi-Fuel Cell

Full cell performance was carried out using a 1 x 1.5" cell made of polycarbonate. The two electrodes were mounted vertically and were separated by Vexar spacers (0.7mm) placed on each side of a Nafion membrane. The flowing electrolyte apparatus consisted of two electrolyte tanks and two flow loops. One tank contained the seawater electrolyte that was pumped to the magnesium anode side. The second electrolyte tank contained seawater, hydrogen peroxide and acid; this electrolyte was pumped to the cathode side of the cell. To maintain constant H₂O₂ concentration, a Masterflex C/L Model 77120-52 micro peristaltic pump was used to meter H₂O₂ into the catholyte reservoir at a fixed rate. A schematic diagram of the magnesium-H₂O₂ SFC is shown in Figure 8.

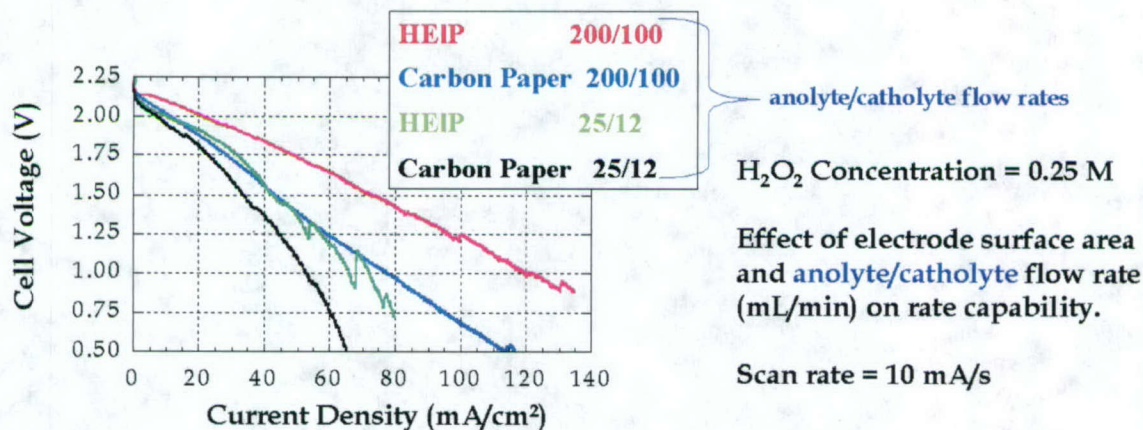
Figure 8 Mg-SFC Schematic Diagram With Planar Carbon Paper And HEIP Cathodes



The catholyte and the electrolyte were pumped into the bottom of the cell, flowed between the anode and the cathode surfaces and the membrane and exited at the top of the cell. The closed loop flowing electrolyte apparatus consisted, in series, of the electrolyte reservoirs, Masterflex L/S MODEL 7518-10 peristaltic pumps, the flow through cell and a return to the reservoir. A EG & G PARC MODEL 362 Scanning Potentiostat in combination with a Nicolet Model 490 Digital Oscilloscope were used to control current and record cell voltage and current relationships. After reduction onto a floppy disc, the data was subsequently downloaded into an EXCEL file for work-up.

The results depicted in Figure 9 show the HEIP SFCs to have significantly better rate capability at both high (200 cm³/min anolyte side; 100 cm³/min catholyte side) and low (25 cm³/min anolyte side; 12 cm³/min anolyte side) flow rates. The polarization performance of the HEIP SFC at low (25/12) flow rate was nearly as good as the planar SFC at high (200/100) flow rate. This is important on a systems basis.

Figure 9 Polarization Curves for Mg-SFC with HEIP and Carbon Paper Cathodes – Varying Flow Rates



The HEIP electrode having the Pd/Ir catalyst deposited by a pulse potential technique performed almost as well as a HEIP cathode with the catalyst deposited by the cyclic voltammetry technique. At low current densities the difference is less than 100mV (Figure 10). A pulse potential deposition of the Pd/Ir catalyst could decrease cathode cost in terms of labor (shorter process) and amount of catalyst.

Figure 10 Polarization Curves for Mg-SFC with HEIP and Carbon Paper Cathodes Pd/Ir - Different Catalysis Techniques

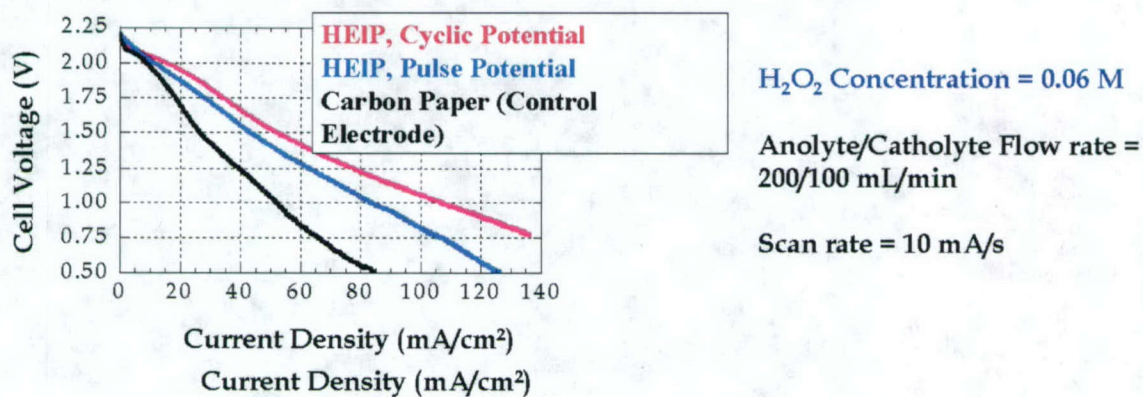
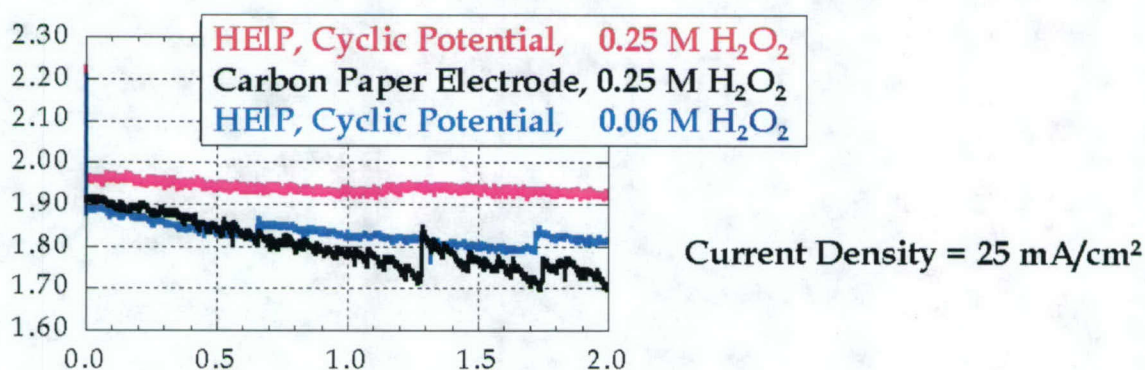


Figure 11 shows the performance of the HEIP SFC at a constant current density of 25 mA/cm² and at different concentrations of H₂O₂ relative to the carbon paper control SFC.

The HEIP SFC developed a higher cell voltage (100mV) at 0.25M H₂O₂ and nearly the same voltage at 4X lower H₂O₂ concentration (0.06M) as the carbon paper SFC. If H₂O₂ concentration can be lowered further, a microporous membrane might replace the presently used ion-exchange membrane with little effect on anode efficiency while significantly decreasing mass transport (cell) resistance. Lower H₂O₂ concentrations will also likely increase H₂O₂ efficiency by decreasing its decomposition rate. Recent experiments have yielded specific energies in the 680 to 730 Wh/kg (Mg alloy plus 50% H₂O₂).

Figure 11 Constant Current Performance of Mg-SFC with HEIP and Carbon Paper Cathodes - Varying H₂O₂ Concentrations



In Summary:

Polarization and constant current results show the high electrolyte penetration (HEIP) electrode significantly improves the rate capability of the Mg-H₂O₂ SFC.

At equivalent concentrations, the HEIP SFCs have significantly better rate capability.

The polarization performance of the HEIP SFC at low catholyte flow rate was nearly as good as the carbon paper control SFC at high flow rate.

The HEIP SFC developed a higher cell voltage at 0.25M H₂O₂ and nearly the same voltage at 0.06M H₂O₂ concentration as the carbon paper SFC.

A pulse potential deposition of the Pd/Ir catalyst offers the advantages of a shorter deposition process and a decrease in the amount of catalyst used.

October 1, 2002 - September 30, 2003 (FY 03)

Technical Objectives

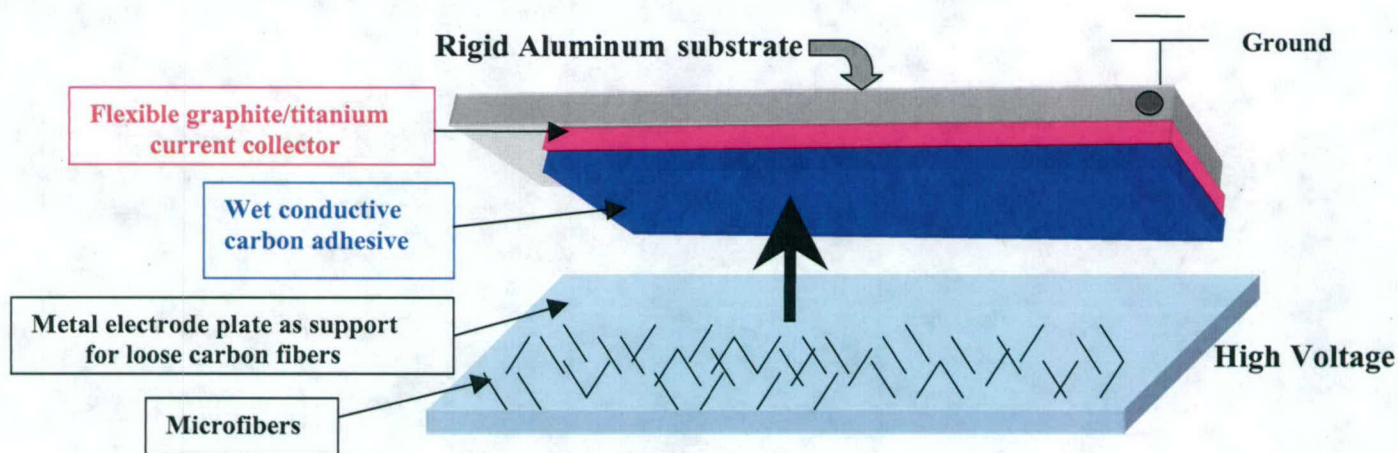
An objective of the present investigations is to improve microfiber array-high electrolyte penetration (HEIP) electrode fabrication technology through the study of novel direct charge and controlled atmosphere (dry air, inert gas, reduced pressure) flocking techniques. Fabrication of carbon microfiber arrays having a two dimensional area greater than 1000 cm^2 , construction of bipolar electrodes, investigation of electrode catalysis, and performance studies of the HEIP electrodes in a magnesium-hydrogen peroxide semi-fuel cell are additional objectives.

Technical Approach

1. Improve catalyzed microfiber array-high electrolyte penetration (HEIP) electrode fabrication technology

Through collaboration with Dr. Yong Kim of the Textile Sciences Department at UMass Dartmouth, a novel modification of the flocking technique process has been tested quite successfully. A rigid aluminum substrate covered sequentially with a flexible graphite or titanium foil collector and a wet conductive carbon adhesive is held above the high voltage electrode with the two electrodes parallel to one another at a fixed distance. The carbon fibers are now placed directly on the high voltage electrode. This new flocking method is pictured in Figure 1.

Figure 1 Schematic Diagram of Direct Flocking Technique



Upon application of the electric field, the fibers are charged directly and propelled upward through the electric field and embed in the wet adhesive normal to the surface of the carbon foil. Thermal curing of the conductive adhesive anchors the fibers to the current collector.

Compared to the indirect charging method of electrostatic flocking, One of the advantages of this technique is that all of the fibers are propelled simultaneously into the electric field. A second advantage is that no shaking is required. Shaking results in a lower percentage of fibers embedded in the adhesive compared to direct charging. In the original technique (corona charging), a non-reproducible percentage of the fibers remained in the hopper even with shaking of the hopper. The fibers can now be weighed and spread evenly over the entire face of the high voltage electrode and the efficiency of the process is more consistent, resulting in reproducible and uniform fiber densities. A third advantage is that the flocking process takes less than 10 seconds. A fourth advantage is that uniformly flocked large surface area carbon microfiber arrays can be prepared. The fabrication of uniform density microfiber arrays greater than 1000 cm^2 was carried out. The fibers of these arrays are then catalyzed with Pd/Ir to form high electrolyte penetration (HEIP) electrodes.

The flocking process is typically carried out at room atmosphere. The effect of water vapor, nitrogen, oxygen and other molecules in the electric field on the flocking of carbon fibers has not been studied. A prototype vacuum chamber for carrying out the flocking process has been constructed in Dr. Kim's laboratory at UMass Dartmouth. Using this chamber, the preparation of carbon microfiber arrays in dry air and in dry nitrogen gas at pressures below one atmosphere was attempted.

2. Fabrication of bipolar electrodes

A bipolar electrode is necessary for the successful deployment of a Mg-H₂O₂ SFC. The electroactive components are a catalyzed cathode for the reduction of H₂O₂ and a metal anode such as Mg. The two must be electrically connected and as close as possible while being isolated from the electrolyte of the other to minimize leakage currents and maximize efficiency. That is, the metal anode must not be exposed to the catholyte and the catalyst must be isolated from the anolyte. The barrier between the anode and the catalyzed cathode must have high electrical conductivity, be chemically inert and nonporous. Graphite foil and titanium foil have been studied. The barrier will be coated on one side with conductive carbon screen printing ink and serve as a support for the carbon fibers that will support the catalyst. The ink will be exposed directly to the peroxide/acid/salt water electrolyte so it must be stable in the low pH, oxidizing environment. The opposite side of the barrier will be coated with an adhesive to bond the catalyst/fibers/ink/foil composite to the anode. This adhesive must have enough cohesive strength to maintain the integrity of the bipolar composite electrode.

3. Electrode catalysis

In an attempt to achieve greater catalysis, lower electrode loading and to reduce catalyst (Pd/Ir) deposition time, pulse potential depositions at various cycles and duration times were investigated. The control conditions were cyclic voltammetry, -0.15 V to -0.30 V, 1.0 mV/s for 25 cycles using a solution of 2.0 mM PdCl₂ and Na₂IrCl₆ with 0.2 M KCl, 0.1 M HCl at 70°C. The electrode substrate was 0.25 mm thick carbon paper. Evaluative parameters were Pd/Ir ratio of 1:1 as determined by EDS, polarization curve onset potential (0.627 V vs. Ag/AgCl for the control), and polarization curve slope (402 mA/V for the control). SEM and EDS were used extensively to evaluate the catalyst morphologies and elemental composition. The linear sweep voltammetry polarization curves were recorded while using 0.5 cm² electrodes and an electrolyte of 0.25 M H₂O₂, 0.2 M H₂SO₄, 40 g/L NaCl at ambient temperature.

4. Performance of HEIP electrodes in a magnesium-hydrogen peroxide semi-fuel cell

Full cell performance will be carried out using 1" x 1.5" and 1.5" x 8.0" dual flowing electrolyte cells. For these test cells, the two electrodes are mounted vertically and are separated by Vexar spacers (0.7 mm thick each) placed on each side of a Nafion membrane. The flowing electrolyte apparatus consists of two electrolyte tanks and two flow loops. One tank contains the sodium chloride electrolyte that is pumped to the magnesium anode side. The second electrolyte tank contains sodium chloride, hydrogen peroxide and acid; this electrolyte is pumped to the cathode side of the cell. The catholyte and the sodium chloride electrolyte are pumped into the bottom of the cell, flow between the anode and the cathode surfaces and the membrane, and exit at the top of the cell. The closed loop flowing electrolyte apparatus consisted, in series, of the electrolyte reservoirs, Masterflex L/S MODEL 7518-10 peristaltic pumps, the flow through cell and a return to the reservoir. Cell voltage and current relationships, individual electrode voltages, as well as catholyte and anolyte pH can be measured. Using Lab View software, data are acquired by computer for subsequent analysis. Direct titration of H₂O₂ is used to monitor the change in its concentration. The magnesium consumption is monitored through mass measurement. Electrochemical percent efficiency for the anode and cathode reactions are then carried out. Quantification of the physical nature of the catalyst surface before and after repeated use is monitored using SEM.

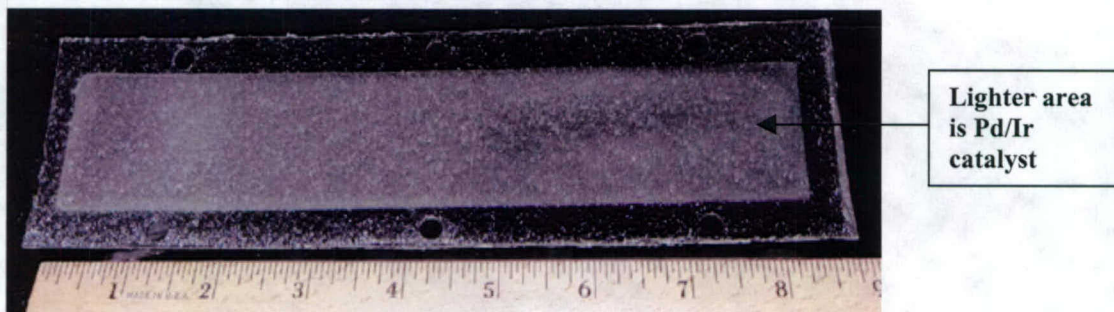
Progress

1. Improve catalyzed microfiber array-high electrolyte penetration (HEIP) electrode fabrication technology

In preparing large area electrodes, it was determined that a field strength of 5kV/cm (defined as the applied voltage per cm of vertical distance between the electrodes of the flocking apparatus) reproducibly yielded uniform distribution of the carbon fibers across the entire area being flocked. These carbon microfiber arrays (CMAs) were then catalyzed with Pd/Ir by electrochemical deposition to give high electrolyte penetration (HEIP) electrodes for the reduction of H₂O₂. Seventy-eight-cm² electrodes (defined as the two dimensional planar area of the current collector) (1.5" x 8.0") were routinely

made with 120,000 to 130,000 fibers per cm. This fiber density is determined by SEM image fiber counting or by weighing the rigid substrate, current collector and adhesive before and after flocking the carbon fibers. Knowledge of the individual fiber volume and the density is required to calculate the fiber density via the weighing method. Figure 2 depicts such an electrode.

Figure 2 Pd/Ir catalyzed HEIP Electrode (1.5"x 8.0")



The flocking efficiency, defined as the weight of fibers held in place by the conductive adhesive divided by the total weight of fibers placed on the high voltage flocking apparatus electrode, was found to vary with electrode size. For the 78cm² electrodes it was between 55 and 60%. The improved performance obtained with these 3D HEIP electrodes has resulted in replacement of carbon paper based Pd/Ir cathodes with HEIP cathodes for the 1.5" x 8.0" Mg/H₂O₂ SFC studies.

A flocking apparatus has been designed to prepare carbon microfiber arrays with a two dimensional planar area greater than 1000 cm². Similar to the smaller area arrays, an electric field strength of 5 kV/cm was used. A very uniform distribution of fibers has been achieved for an array with an area above 1100cm². The flocking apparatus and the electrode are pictured in Figure 3A & B, respectively.

Figure 3A Large Area Flocking Apparatus

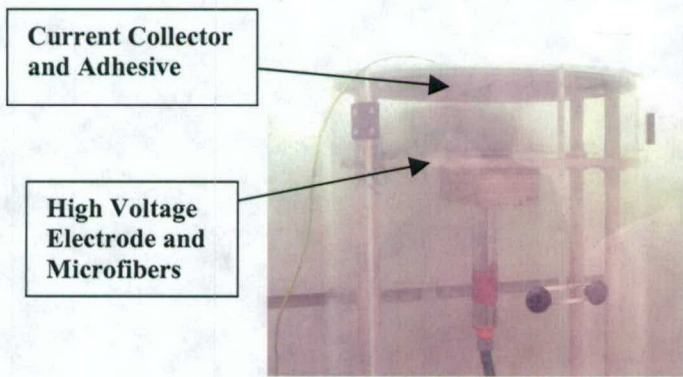


Figure 3B Large Area Carbon Microfiber Array

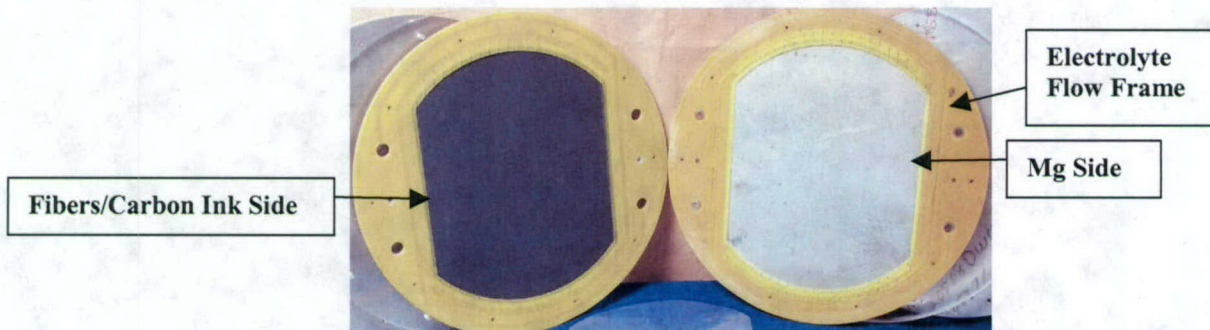


The flocking processes under dry air and inert nitrogen atmosphere at reduced pressure have been investigated. The reduced pressures and associated applied voltages required for proper functioning of the flocking apparatus have been established. Carbon fiber arrays have been prepared. SEM imaging is planned to determine if improved array morphology has been attained.

2. Fabrication of bipolar electrodes

Bipolar electrode fabrication, necessary for the successful deployment of a Mg-H₂O₂ SFC, has been studied. Graphite foil was shown to be not totally impervious to the electrolyte. The acidic H₂O₂ catholyte traversed the graphite barrier leading to a direct reaction of the acid and the H₂O₂ with the Mg anode. High purity titanium foil (Hamilton Precision Metals Grade I, 125 μm thick) has proven to be a good barrier material. It is nonporous, has good electrical conductivity, and is chemically inert in the timeframe of our experiments. The carbon screen printing ink (Creative Materials 112-48) has shown excellent stability in the low pH, oxidizing environment that is the hydrogen peroxide/sulfuric acid/sodium chloride catholyte. Carbon ink and carbon epoxy have proven to be inadequate as adhesives to bind the Ti barrier to the Mg anode. Some success has been achieved with a conductive double sided tape obtained from 3M(#9703). A large area bipolar electrode incorporating fibers/carbon ink/titanium foil/conductive double sided tape/magnesium has been fabricated and is depicted in Figure 4. Stability studies on this method of bipolar construction as a function of temperature are currently under way.

Figure 4 Large Area Bipolar Electrode Assembly



3. Electrode catalysis

Pulse potential depositions were investigated to achieve improved catalysis, lower electrode loading, and a reduction in the time of deposition compared to the control Pd/Ir deposition conditions. The results are summarized in Table I.

Increased delay times at the more positive potential (-0.15V) were used to provide time for the concentration gradient established at the electrode solution interface at -0.3V to be eliminated. Some conditions yielded improved polarization curve slopes while other conditions gave more positive onset potentials. The reduction in time of deposition relative to the control (125min.) provided by the pulse potential technique is clearly evident. Instrumentation is being assembled to allow for deposition times shorter than 0.1s which is the lower limit of the current instrument. Shorter delay times will allow for even greater reduction in deposition time and allow for higher ratios of delay times at the two potentials (5:1 to 30:1 ratios shown in Table I) while not exceeding the control deposition time.

Table I Pd/Ir Catalysis

Pulse Conditions		#Cycles	Polarization Slope ^a mA/Vcm ²	OCV ^b volts	Deposition Time min.
Delay Time, s at -0.15 V	Delay Time, s at -0.30 V				
0.5	0.1	4000	482	0.619	40.0
1.5	0.1	4000	411	0.620	106.7
2.5	0.1	2000	385	0.646	86.6
3.0	0.1	2000	152	0.659	103.3

^a LSV @ 100 mV/s; 0.5 cm² electrode area; 0.25 M H₂O₂; 0.2 M H₂SO₄; 40 g/L NaCl; 20 °C

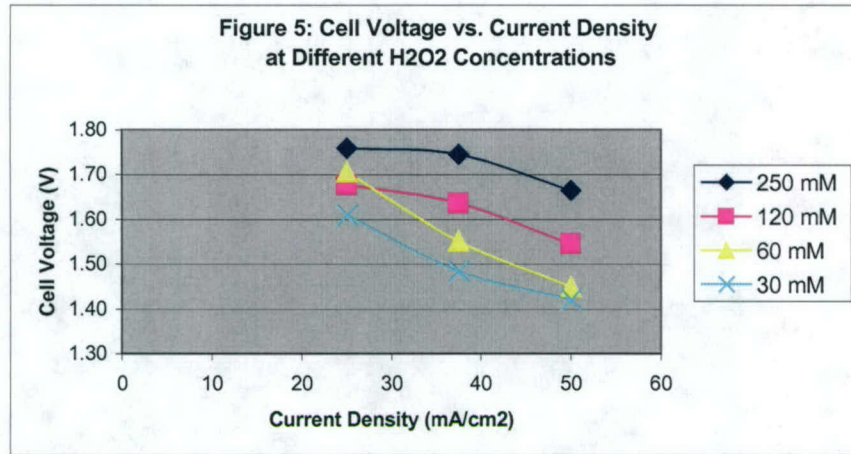
^b Volts vs Ag/AgCl

Control Conditions: CV Polarization slope=402 mA/cm²; OCV=0.627 V vs Ag/AgCl

SEM images confirm that the Pd/Ir nodules formed by pulse potential deposition are similar to those obtained by the cyclic voltammetry method. The EDS mapping shows uniform distribution of the palladium and iridium on the surface of the carbon fibers. The EDS spectrum yields peak heights for the Pd and Ir that are indicative of a 1:1 atomic ratio of Pd and Ir in the deposit. X-ray diffraction will be performed to further probe the composition of the catalyst deposit.

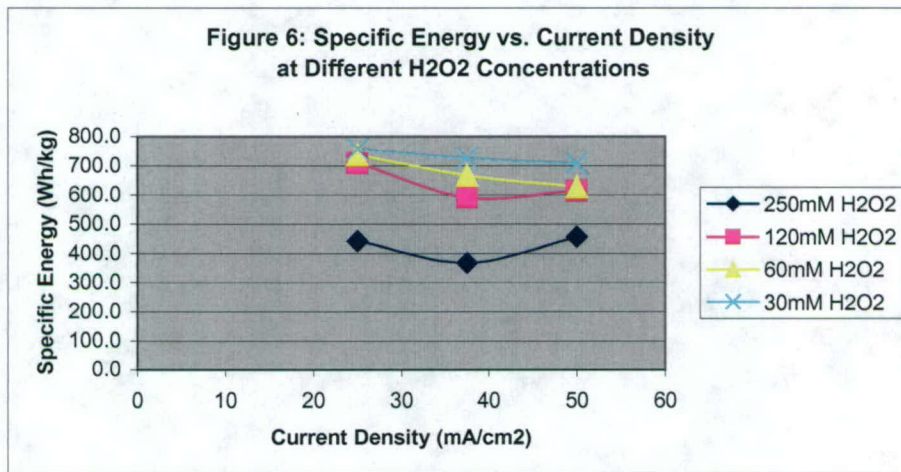
4. Performance of HEIP electrodes in a magnesium-hydrogen peroxide semi-fuel cell

Results obtained to date using the 1.0" x 1.5" test cell show the SFC cell voltage with the HEIP cathode in place was lowest at 30 mM H₂O₂ at the three current densities studied (25, 37.5 and 50.0 mA/cm²). Successive increases in cell voltage were observed at the three current densities as the H₂O₂ concentration was increased from 30 to 60, 120, and 250 mM. This data is summarized in Figure 5.



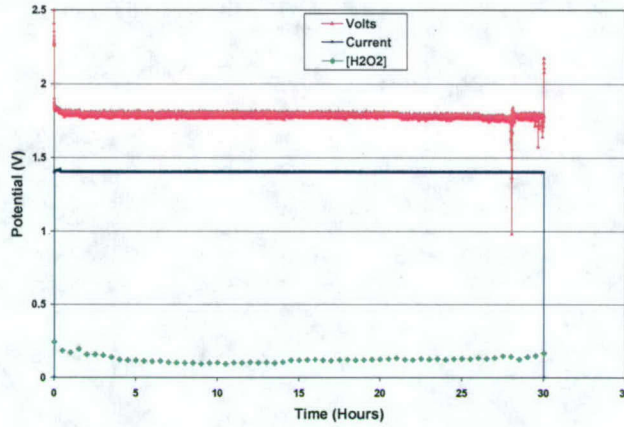
When compared to the “planar” catalyzed carbon foil control electrode, potential improvement for the HEIP electrode was observed at all current densities and concentrations of H₂O₂. This potential improvement is greatest at the 30 mM concentration level.

As the concentration of H₂O₂ was increased, a decrease in the electrochemical efficiency of H₂O₂ was also observed. This decrease in efficiency is reflected dramatically when the specific energy (Wh/(Kg of reactants Mg + H₂O₂)) is plotted versus the current density. Figure 6 shows that the highest specific energies were observed at 30 mM H₂O₂. Generally, the specific energy decreases with an increase in concentration of H₂O₂.



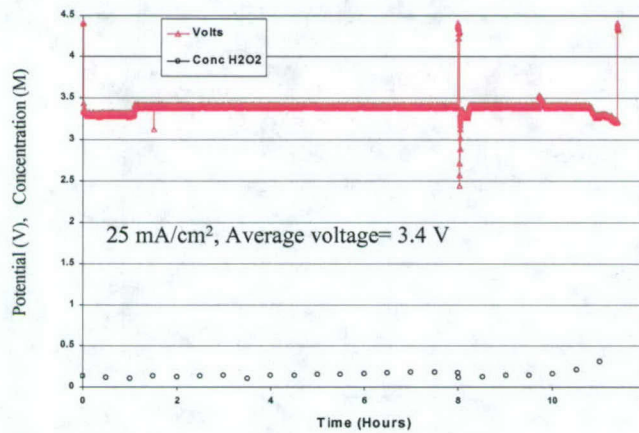
SFC cell performance for a 78 cm² HEIP electrode (1.5” x 8.0” test cell) over a thirty hour time period is shown in Figure 7. A very steady cell voltage of 1.7 V was recorded at 25 mA/cm² current density with an H₂O₂ concentration averaging 100 mM.

Figure 7 Long Duration SFC Performance with HEIP Cathode



The 1.5" x 8.0" test cell was modified to permit incorporation of a bipolar electrode. The performance of a two-cell stack with this bipolar electrode is shown in Figure 8. An average 1.7 V per cell, 3.4 V for the two cell stack, was observed over a 10 hour period with an H₂O₂ concentration averaging 100 mM. Restart capability was also demonstrated as the cell stack was shut down at the 8 hour mark and restarted the following day.

Figure 8 Two Cell Stack Performance with Bipolar Electrode Configuration



October 1, 2003 - September 30, 2004 (FY 04)

Technical Objectives

An objective of the current investigations is to improve carbon microfiber array architecture through optimization of carbon fiber density, fiber length and thickness of conductive adhesive. Other objectives include studies of millisecond pulse potential deposition techniques for the Pd/Ir H₂O₂ reduction catalyst, determination of the electrochemically active area of the new **high electrolyte penetration (HEIP)** electrodes, development of a model to gain a deeper understanding of the relationships among fiber density, flow of electrolyte, the current and the voltage across the forest of catalyzed fibers that comprise the electrode surface, and evaluation of the performance of these cathodes toward H₂O₂ reduction under operating conditions to be used in full cell applications.

Technical Approach

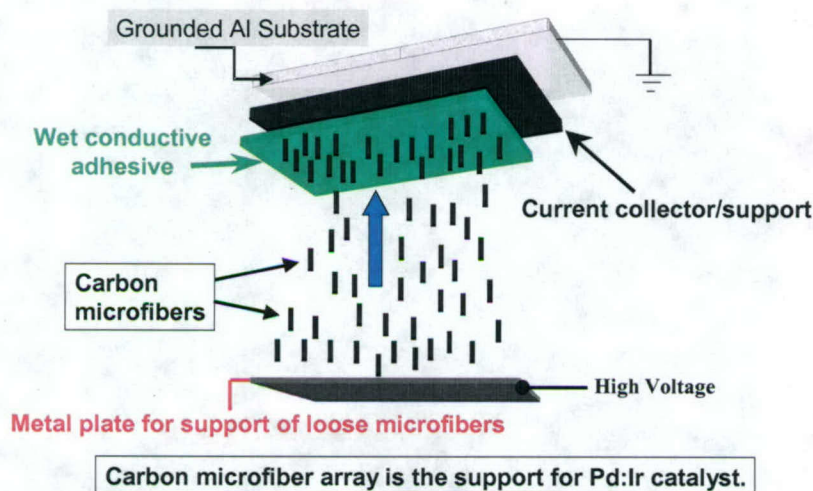
I. Improve catalyzed carbon microfiber electrode architecture

A novel modification of the flocking technique process has been implemented quite successfully. A rigid aluminum substrate covered sequentially with a flexible graphite collector and a wet conductive carbon adhesive is held above the high voltage electrode. The two electrodes are parallel to one another at a fixed distance. The carbon fibers are placed directly on the high voltage electrode. Upon application of the electric field, the fibers are charged directly and propelled upward through the electric field and impact normal to the surface of the carbon foil. These fibers are held in place by the conductive adhesive. This new direct flocking method and operating parameters are pictured in Figure 1.

One of the advantages of this technique is that all of the fibers are propelled into the electric field. A second advantage is that the fibers can now be weighed and spread evenly over the entire face of the high voltage electrode. This advantage should provide for greater reproducibility in electrode carbon fiber density. A third advantage is that the flocking process takes less than 10 seconds. The fibers of these arrays are then catalyzed with a palladium/iridium alloy to form **high electrolyte penetration (HEIP)** electrodes.

Figure 1

**Preparation of Carbon Microfiber Array:
Electrostatic Flocking**



- 1) Load Carbon fibers onto metal support by mass
Pitch based, 0.5mm length, 10 μ m diameter
- 2) Electrode to substrate distance: 10-30 cm
- 3) Applied Voltage: 30-100 kV
- 4) Accelerate fibers through electric field into wet ink.
- 5) Flocking time < 10s
- 6) Thermally cure conductive adhesive

Optimization of the carbon fiber density and fiber length will be carried out. Methods of reproducibly and quantitatively distributing the carbon fibers on the high voltage plate of the flocking apparatus will be studied. . Dr. Yong Kim of the UMass Dartmouth Textile Sciences Department, with whom we have collaborated on the flocking process, has acquired a fiber cutting instrument. We now have readily available a tool to cut a fiber tow (i.e. a strand of 12,000 fibers that is variable in length) to any desired length (0.25mm minimum length) with better control of the cutting precision and much shorter turn around time.

The flocking process is typically carried out at room atmosphere. The effect of water vapor and air in the electric field on the flocking process has not been thoroughly assessed. A prototype vacuum chamber for carrying out the flocking process is available for our use in the laboratory of Dr. Yong Kim. Preparation of carbon microfiber arrays in dry air, nitrogen-air mixtures, or in a more conductive medium such as in sulfur hexafluoride at atmospheric or reduced pressure will be attempted.

II. Electrode Catalysis

New pulse potential deposition schemes using very short pulse times (10ms-100ms) will be devised to decrease the size of the catalyst nodules, increase the total carbon fiber area covered by the catalyst, and to reduce the catalyst loading. Previously pulse duration times less than 100ms were not possible. The appropriate data acquisition I/O card has been acquired and a Lab View software program has been written to carry out pulse potential deposition of the Pd/Ir catalyst. The pulse widths, the voltages to which the pulses will be made, and the number of cycles are variable for a given experiment. Initially the potential limits will be those used for the baseline cyclic voltammetry deposition technique (-0.150V to -0.300V vs Ag/AgCl). Pulse widths at the more positive potential (-0.150V) will be longer than those at the more negative potential (-0.300V) to allow bulk concentration to be reestablished at the electrode surface thus eliminating concentration polarization. Short pulse widths and various pulse width ratios (e.g. 5:1 to 50:1) will be explored. Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometry (EDS) and X-ray Diffraction (XRD) will be used to monitor cathode morphology and composition.

Because the electrode is a composite of carbon or titanium foil, carbon ink, carbon fibers, and Pd/Ir catalyst, BET surface area determinations are not applicable for the determination of the electrochemically active area of a HEIP electrode. Rotating disk electrode (RDE) and cyclic voltammetry (CV) experiments will be explored using the well characterized electrochemical couple ferricyanide $[\text{Fe}(\text{CN})_6^{3-}]$ / ferrocyanide $[\text{Fe}(\text{CN})_6^{4-}]$. Application of the appropriate equations, Levich equation for RDE and Randles-Sevcik equation for CV experimentation, will be used to determine the active surface area.

III. Microfiber Cathode Performance Studies

Performance evaluation of the newly fabricated carbon microfiber arrays catalyzed under optimum conditions of the pulse deposition technique will be carried out. These studies will use a flowing H_2O_2 catholyte half-cell and a seawater anolyte half-cell having a cell gap (0.75mm) and electrode area of either 7.0cm^2 (1.0" x 1.5" test apparatus) or 77cm^2 (1.5" x 8.0" test apparatus) similar to the full cell test apparatus used successfully in previous investigations. The capability also exists with the test apparatus to make individual electrode voltage measurements using a Ag/AgCl reference electrode and a Luggin-Haber capillary. The catholyte containing seawater, hydrogen peroxide and acid will be pumped into the bottom of the half-cell, flow across the cathode surface and exit at the top. The closed loop flowing electrolyte apparatus will consist, in series, of the catholyte reservoir, a peristaltic pump, a micro-pump to maintain H_2O_2 concentration, a second micro-pump to maintain acid concentration, the flow through the cathode half-cell and a return to the reservoir. The seawater anolyte flows from the reservoir through a peristaltic pump to the bottom of the anode half-cell, across the anode surface, exits at the top of the cell, and returns to the anolyte reservoir. Polarization and constant current

tests at low and high current densities will be used to investigate electrode and full cell potential, electrochemical efficiency, gassing rate, durability and stability with time. Using Lab View software, data are acquired by computer for subsequent analysis.

An understanding of the interaction of the electrochemical kinetics, the catholyte concentration profile, any gassing that occurs due to H_2O_2 decomposition, the fiber length, fiber density, and the fluid dynamics cannot be obtained solely from experiments because of the complexity involved. A predictive model will be developed to optimize the overall performance. Ultimately, the model will play an important role in the development of efficient electrolyte management systems. The modeling work is being carried out in collaboration with Dr. Wilson Chiu of the University of Connecticut.

Progress

I. Improve catalyzed carbon microfiber electrode architecture

Uniform distribution of carbon fibers was attained on the high voltage steel plate of the direct flocking apparatus using a sifting device fabricated in our laboratory. This device consisted of a polypropylene macroporous mesh, 297 μm opening size and 420 μm thickness, held tightly on a one inch wooden frame by means of a groove and spline. The dimensions of 2.0" x 9.0" covered the entire area of a 1.5" x 8.0" electrode with an 0.25" overlap around the circumference of the electrode. With the polypropylene mesh facing down, the device was filled with carbon fibers and a tapping method was used to discharge the fibers. Good uniform distribution and excellent reproducibility was achieved. Approximately 3.0 mg of fibers were discharged per tap. For four successive trials the average weight of fibers discharged was 335mg with a standard error of 3.0 mg or a relative uncertainty of 0.9%. The average flocking efficiency, the weight of fibers imbedded in the conductive ink of the carbon microfiber array divided by the weight of fibers on the high voltage plate, was 75% with a standard error of 1.2%.

The cutting of a carbon fiber tow (i.e. a strand of 12,000 fibers) causes the cutting blade of the instrument available in Dr. Yong Kim's laboratory at UMass Dartmouth to become dull in 10 to 15 minutes. New hardened steel, precision ground and polished blades are being manufactured for our use. Completion of the manufacturing of the blades is expected by the end of September. Better control of the cutting precision and a short turn around time for preparing fibers of various lengths (0.75mm, 1.0mm and 1.5mm lengths are planned) will be readily available.

Fabrication of carbon microfiber arrays (CMAs) using progressive field strength stages of 10kV, 30kV and 50kV and 10 kV, 15 kV, and 20 kV applied across the 10 cm gap of the flocking apparatus was investigated. No improvement in CMA architecture was obtained with these progressive field strengths relative to CMAs prepared by using a single field strength.

Preparation of CMAs in dry air and in nitrogen-air mixtures at atmospheric and reduced pressures in the prototype vacuum chamber for carrying out the flocking process available at UMass Dartmouth yielded no improvement in CMA architecture relative to CMAs prepared at atmospheric pressure and ambient laboratory air.

Typically the flocking process is performed in air. Sulfur hexafluoride (SF_6) instead of air was investigated as the flocking medium. SF_6 significantly increases electric field strength and fiber density. This is because SF_6 has a high dielectric strength (80 kV/cm) relative to air (30 kV/cm) at 1 atmosphere pressure. A vacuum flocking chamber at UMASS Dartmouth (UMD) was used for this purpose. The chamber was evacuated to 29+ inches of mercury (removing the air) and then refilled with SF_6 to 1 atmosphere pressure.

The adhesive coated substrate and loose fibers (on conductive support) were placed in the flocking chamber before it was evacuated and refilled with SF_6 . The distance between the electrodes was 10 cm. The length of the fibers was 0.5 mm and the diameter was 0.011 mm. Experiments were performed at 50 kV and 75 kV, field strengths of 5 and 7.5 kV/cm respectively. Fiber densities at these field strengths were 261,000 fibers/cm² (5 kV/cm) and 443,000 fibers/cm² (7.5 kV/cm). In contrast, the maximum field strength achieved in flocking experiments using air as the dielectric at ambient (approximately 1 atmosphere) pressure is 5.0 kV/cm and the maximum fiber density under these conditions is 150,000 fibers/cm². A patent disclosure titled "Method for Increasing Fiber Density in Electrostatic Flocking" has been submitted.

Most recently, Drs. Charles Patrissi and Louis Carreiro of the NUWC chemistry laboratory have successfully grown nanotubes onto carbon microfibers using a combination of electrochemistry and chemical vapor deposition. Further work on optimizing the process will be carried out. Afterward, deposition of the Pd/Ir catalyst on these composite arrays will be explored. Uniformity of coverage, degree of adhesion to the nanotubes and fibers and extent of loading will be explored. The electrochemical performance of cells incorporating the newly fabricated catalyzed composite carbon nanotube/microfiber arrays will be investigated in an effort to maximize voltage and electrochemical efficiency, while maintaining a minimal H_2O_2 concentration.

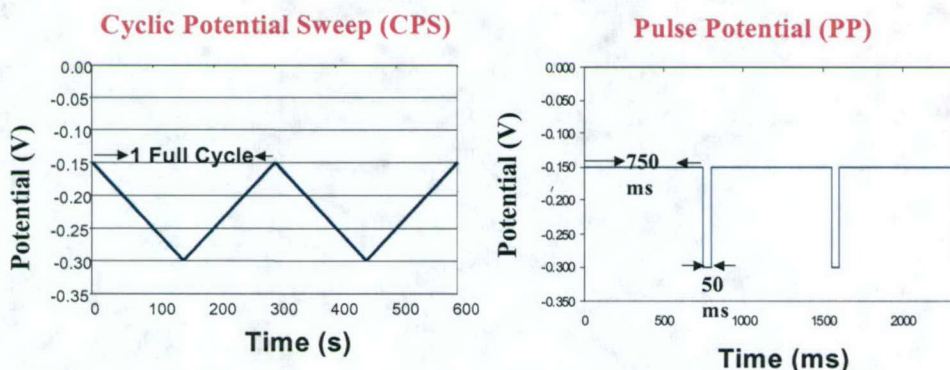
II. Electrode Catalysis

A data acquisition and potentiostat control system was developed from commercially available hardware and software to achieve a pulse potential technique for the deposition of the palladium/iridium alloy catalyst onto the carbon fibers of an array fabricated by the direct charging flocking method. This system consists of a National Instruments data acquisition card having 100 ks/s rate acquisition capability with an analog output connected to the "cell external input" of a PAR model 273A Potentiostat.

Using LabView, software was used to control the potential, the pulse width, and the number of cycles. This system allows the number of cycles and the potentials to which

the pulses are made to be varied and controls pulse widths to as short as 10 ms. Initially the potential limits were those used for the baseline cyclic voltammetry deposition technique. Various pulse width ratios at the potential limits (e.g. 5:1 to 50:1) have been explored. A comparison of the baseline cyclic voltammetry technique and the pulse potential technique is presented in Figure 2.

Figure 2
Catalyst Deposition Techniques



Deposition solution: 2mM PdCl₂, 2mM Na₂IrCl₆, 0.2M KCl, 0.1M HCl

Setup: 3 Electrode Cell; Carbon Fiber WE; Ag/AgCl RE; Carbon Rod AE

A significantly different morphology results from pulse potential (PP), i.e. more uniform and complete fiber coverage than with the cyclic potential sweep (CPS) method. Catalyst loading is equivalent to that obtained by CPS and the deposition time has been decreased by greater than 50%. The morphology typically obtained by CPS is shown in Figure 3A and that obtained by PP in Figure 3B.



Figure 3A. Cross Section of CPS Catalyzed Carbon Microfiber Electrode

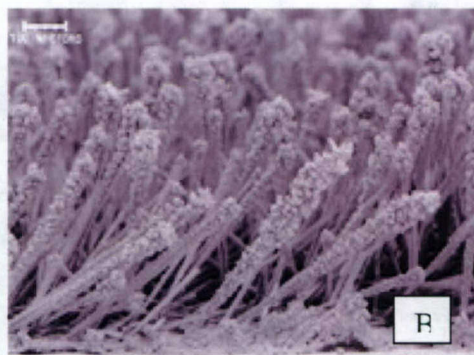
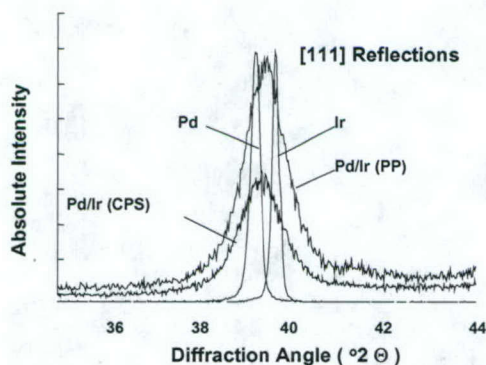


Figure 3B. Cross Section of PP Carbon Microfiber Electrode

The catalyst deposit obtained by cyclic potential sweep has been shown to be a single phase alloy having a 1:1 atomic ratio of palladium to iridium. XRD data for the CPS-deposited catalyst along with that for the PP-deposited catalyst is shown in Figure 4. The symmetrical shape and position of the [111] reflections for the PP and CPS catalysts, centered at approximately $40^\circ 2\theta$ midway between the reference peaks of palladium and iridium, confirm uniform alloy formation occurs in both deposition techniques. Furthermore, cell refinement calculations, based on cubic symmetry, give a lattice parameter "a" for the PP catalyst (3.894Å) that is similar to that obtained for the CPS catalyst (3.899Å). One can conclude that the PP technique yields a homogeneous alloy of palladium and iridium similar to that produced by CPS.

Figure 4



The magnesium-hydrogen peroxide cell performance incorporating a cathode catalyzed by cyclic potential sweep was compared to the performance of a cell having a cathode of similar fiber density catalyzed by pulse potential. The polarization curves for these two cases show no significant difference in performance.

Rotating disk electrode (RDE) and cyclic voltammetry (CV) experiments were explored using the well characterized electrochemical couple ferricyanide $[\text{Fe}(\text{CN})_6]^{3-}$ / ferrocyanide $[\text{Fe}(\text{CN})_6]^{4-}$ for the determination of the electrochemically active area of the catalyzed carbon microfiber electrodes. Application of the appropriate equations, Levich equation for RDE and Randles-Sevcik equation for CV experimentation, were used to determine the area. A baseline was established using a 0.100 M KCl solution. A straight baseline with a potential window from 0.75V to -0.10V vs Ag/AgCl was obtained. A 4.0 mM $\text{K}_3\text{Fe}(\text{CN})_6$ (potassium ferricyanide), 0.100 M KCl mixture was used for the area determination. A diffusion coefficient value of $7.62 \times 10^{-6} \text{ cm}^2/\text{s}$ at 25°C in the solution medium employed is listed in Sawyer, Sobkowiak and Roberts Jr., "Electrochemistry for Chemists", p 219 as the accepted value and was the value used in our calculations. Reasonable data was obtained using linear scan voltammetry on a quiet solution deaerated with argon and blanketed with Ar during the trials. For a seven cm^2 two dimensional area catalyzed carbon microfiber electrode, an average electrochemical area of $2.10 \times 10^3 \text{ cm}^2$ with a standard error of $0.12 \times 10^3 \text{ cm}^2$ was obtained for five trials. Confirmation of the area by rotating disk electrode (RDE) measurements has not been

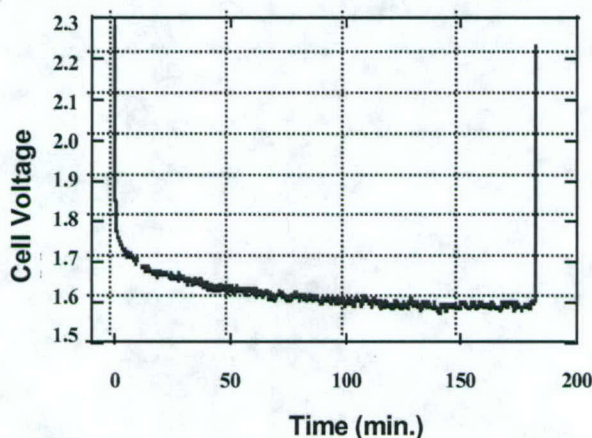
successful. Since the fibers are not completely perpendicular to the surface, there is in fact some crossover of fibers, establishment of a diffusion layer at the electrode solution interface has apparently not been achieved. Additional experimentation is ongoing.

III. Microfiber Cathode Performance Studies

Magnesium-hydrogen peroxide semi-fuel cell performance tests at $25\text{mA}/\text{cm}^2$ and 60mM H_2O_2 using carbon microfiber electrodes catalyzed by cyclic potential sweep (CPS) and by pulse potential (PP) for a three-hour period revealed no significant difference in average cell voltage (1.69V for CPS vs 1.63V for PP) and power density ($42\text{mW}/\text{cm}^2$ for CPS vs $41\text{mW}/\text{cm}^2$ for PP).

The performance over time of a catalyst prepared by pulse potential was examined. The cell voltage-time profile shown in Figure 5 demonstrates the stable voltage obtained. A second three-hour trial with the same cathode at the same current density and concentration of H_2O_2 yielded a very similar voltage-time profile. The average cell voltages for the first and second trials were 1.63V and 1.61V respectively.

Figure 5. Performance Over Time for Cathode Catalyzed by PP



The effect of carbon array fiber density at similar catalyst loading was investigated. A cathode having 168×10^3 fibers/ cm^2 and $11.1\text{mg}/\text{cm}^2$ Pd/Ir was compared with an array having 62×10^3 fibers per cm^2 and $11.5\text{mg}/\text{cm}^2$ Pd/Ir. Assuming fairly uniform distribution of catalyst on the fibers, the electrode with the lower fiber density has more catalyst per fiber ($0.2\mu\text{g}/\text{fiber}$ vs $0.07\mu\text{g}/\text{fiber}$). The performance of the electrode with the lower fiber density shows improved performance of 40mV over the entire 3 hour time period of the test. This may indicate better access to the catalyst by the H_2O_2 catholyte at the reduced fiber density. Further investigations are being carried out.

Electrodes having 125×10^3 to 140×10^3 fibers per cm^2 and 0.5 mm length fibers have typically achieved average voltages in a Mg- H_2O_2 cell in the 1.65V to 1.70V range. An electrode with 87×10^3 fibers per cm^2 and 0.75 mm length fibers with a catalyst loading per two dimensional cm^2 ($8\text{mg}/\text{cm}^2$) similar to that of the higher fiber density electrodes has shown significantly better performance. An average voltage of 1.80V was obtained. This represents an increase of 100 to 150 mV over the test duration. Fiber length relative to half-cell gap as well as better access to the catalyst may play a role. Additional tests are planned.

Using our capability with the test apparatus, individual anode and cathode voltage measurements vs a Ag/AgCl reference electrode as a function of current density have been made. The magnesium anode polarizes by 0.130V from open circuit to a current density of $100 \text{ mA}/\text{cm}^2$. The Pd/Ir catalyzed carbon microfiber cathode polarizes by a very significant 1.49V toward the reduction of H_2O_2 from open circuit to $100 \text{ mA}/\text{cm}^2$. At $25\text{mA}/\text{cm}^2$, a typical operating current density for the cell, the anode polarization was measured at 0.060V while the cathode polarization was 0.43V. Clearly the efforts to improve the electron transfer process, i.e. to reduce the concentration and kinetic polarization, at the cathode would lead to noteworthy gains in cell voltage for the Mg- H_2O_2 semi-fuel cell.

Catalyzed carbon microfiber array performance modeling has been undertaken. Variables considered have been fiber density, reduction rate, electrochemically active area, H_2O_2 concentration and flow rate. A first approximation contour plot of H_2O_2 mass fraction (Y axis) with flow direction (X axis) and across the electrode face (Y axis) has been constructed. A streamwise velocity plot for different porosities has also been created. The velocity is plotted for the channel center while the streamwise variable x is scaled with the channel width. Cell potential vs current density model plots validate well against experimental data obtained with our 1.0" x 1.5" Mg-SFC test apparatus at the 60 mM and 120 mM hydrogen peroxide levels. The 30 mM and 250 mM cases had larger deviation. The model needs to be refined to better account for activation and ohmic polarization. In this regard, a fixture is being devised to obtain voltages at specific intervals across the face of the cathode at various current densities. The model will also be refined based on additional electrochemically active area and carbon fiber density measurements.

Refereed Journal Articles

1. Bessette, R.R., Patrissi, C.J., Medeiros, M.G., Carreiro, L.G., Deschenes, C.M., Dunnell, M.M., and LaFratta, C.N., "The Application of Novel Microfiber Carbon Electrodes to Magnesium-Hydrogen Peroxide Semi Fuel Cells", Proceedings, 40th Power Sources Conference, pp 355-358, June 2002
2. Bessette, R.R., Arruda, T.M., Patrissi, C.J., Tucker, S.P., Carreiro, L.G., Medeiros, M.G., and Deschenes, C.M., "Catalysis, Architecture and the Electrochemical Performance of Microfibrous Cathodes for Hydrogen Peroxide-Based Fuel Cells, Proceedings, 41st Power Sources Conference, pp 424-427, June 2004
3. Medeiros, M.G., Bessette, R.R., Patrissi, C.J., Deschenes, C.M., Carreiro, L.G., Tucker, S.P. and Atwater, D.W., "Magnesium-Solution Phase Catholyte Semi-Fuel Cell for Undersea Vehicles", J. Power Sources, **136 (2)**, 226-231, 2004

Presentations

1. R.R. Bessette, C. Patrissi, M. Medeiros, C. LaFratta, C. Deschenes, "Carbon Microfiber High Electrolyte Penetration (HELP) Electrodes", 2002 AFOSR/ONR Electrochemistry Review, Annapolis, MD, March 4-6, 2002
2. Bessette, R.R., Patrissi, C.J., Medeiros, M.G., Carreiro, L.G., Deschenes, C.M., Dunnell, M.M., and LaFratta, C.N., "The Application of Novel Microfiber Carbon Electrodes to Magnesium-Hydrogen Peroxide Semi Fuel Cells", 40th Power Sources Conference, Cherry Hill, NJ, June 12, 2002
3. Bessette, R.R., Patrissi, C.P., Kim, Y.K., Dunnell, M.M., Gomes, D.P., and Arruda, T.M., "Catalyzed Carbon Microfiber Electrode Development for Semi-Fuel Cell Applications", AFOSR/ONR Electrochemical Science and Technology Review, Annapolis, MD, March 3-5, 2003
4. Medeiros, M.G., Bessette, R.R., Dow, E.G., "Magnesium Anode Seawater/Acid/Catholyte Electrolyte Utilizing a Palladium and Iridium Carbon Paper Cathode Electrochemical System", Fuel Cells 2003 Third Annual BCC Conference, Stamford, CT, March 30, 2003
5. Patrissi, C.J., Bessette, R.R., Kim, Y.K., Dunnell, M.M., Gomes, D.P., Arruda, T.M., "Fabrication and Electrochemical Performance of High Surface Area Catalyzed Carbon Fiber Cathodes", 203rd Meeting of the Electrochemical Society, Paris, France, May 1, 2003
6. Arruda, T.M., Gomes, D.P., Dunnell, M.M., Bessette, R.R., Patrissi, C.J., "Fabrication and Performance of High Surface Area Carbon Fiber Cathodes in a Magnesium-Hydrogen Peroxide Semi-Fuel Cell", 9th Annual Sigma Xi Research Exhibit, University of Massachusetts Dartmouth, May 6,7, 2003

7. Medeiros, M.G., Bessette, R.R., Deschenes, C.M., Patrissi, C.J., Carreiro, L.G., Tucker, S.P., and Atwater, D.W., "Magnesium-Solution Phase Catholyte Semi-Fuel Cell for Undersea Vehicles", 23rd International Power Sources Conference, Amsterdam, Netherlands, Sept. 24, 2003

8. Bessette, R.R., Patrissi, C.J., Dunnell, M.M., Arruda, T.M., and Gomes, D.P., "Performance Studies of 3D High Surface Area Catalyzed Carbon Microfiber Cathodes in a Magnesium-Hydrogen Peroxide Semi-Fuel Cell", 204th Meeting of the Electrochemical Society, Orlando, FL, Oct. 16, 2003

9. Bessette, R.R., Arruda, T.M., "High Surface Area Semi-Fuel Cell Cathode Development", ONR Workshop on Fuel Cells for Unmanned Undersea Vehicles, Newport, RI, Oct., 30, 2003

10. Bessette, R.R., Arruda, T.M., Patrissi, S.P., Carreiro, L.G., Medeiros, M.G., Deschenes, C.M. and Tucker, S.P., "Catalysis, Architecture and the Performance of Catalyzed Carbon Microfiber Cathodes", 2004 AFOSR/ONR Electrochemistry Program Review Conference, Annapolis, MD, April 19,20,2004

11. Arruda, T.M., Bessette, R.R., Patrissi, C.J., Carreiro, L.G., Medeiros, M.G., Deschenes, C.M. and Tucker, S.P., "Catalysis, Architecture and the Performance of Catalyzed Carbon Microfiber Cathodes for Hydrogen Peroxide-Based Fuel Cells, 10th Annual Sigma Xi Research Exhibit, University of Massachusetts Dartmouth, April 27,28, 2004

12. Bessette, R.R., Arruda, T.M., Patrissi, C.J., Tucker, S.P., Carreiro, L.G., Medeiros, M.G., and Deschenes, C.M., "Catalysis, Architecture and the Electrochemical Performance of Microfibrous Cathodes for Hydrogen Peroxide-Based Fuel Cells", 41st Power Sources Conference, Philadelphia, PA, June 16, 2004