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Development and characterization of a novel carbon fiber based cathode for semi-fuel cell applications

Russell R. Bessette^{a,b,*}, Maria G. Medeiros^b, Charles J. Patrissi^b,
Craig M. Deschenes^{b,c}, Christopher N. LaFratta^{a,b}

^aUniversity of Massachusetts Dartmouth, N. Dartmouth, MA 02747, USA

^bNaval Undersea Warfare Center, Newport, RI 02841, USA

^cBAE Systems, Middletown, RI 02842, USA

Abstract

Fabrication of a microfibre carbon electrode (MCE) using a textile science flocking technique is described. Carbon fibers, 0.5 mm long and 10 μm in diameter are aligned perpendicular to the surface of a conductive carbon epoxy coated carbon paper substrate in a high voltage (typically 70 kV) field. SEM images are used to confirm high carbon fiber density and associated high volumetric surface area. Coverage of the carbon fiber surface with stable Pd–Ir clusters is shown. Performance of the MCE in a magnesium–hydrogen peroxide semi-fuel cell (SFC) under optimum conditions and at reduced concentration of H_2O_2 is reported upon. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Development of affordable, safe and environmentally compatible energy sources for unmanned undersea vehicle (UUV) propulsion continues to attract a great deal of interest. Aluminum and magnesium anodes [1] have received considerable attention due to their high standard potentials and Faradaic capacity [2]. Their application to UUVs is of particular interest due to the availability of seawater to act as an electrolyte or catholyte solvent. This to further enhance their effectiveness as an energy source on a systems basis.

Semi-fuel cell (SFC) technology refers to the use of a solid reductant anode (e.g. aluminum or magnesium) and a soluble oxidant (e.g. H_2O_2) dissolved in the electrolyte to form a catholyte, which is metered into the cell as required. These new solution phase systems should be capable of performing as high energy density sources, providing a broad power turn-down ratio; making them useful for torpedo propulsion. They may, however, be better suited for the low power/long endurance applications of UUVs. This paper focuses on the development of microfibre carbon electrodes (MCEs) for the solution phase of SFC systems possessing low rate, very long endurance capabilities.

The combination of aluminum metal and hydrogen peroxide as an energy source has been studied extensively. Scamans and coworkers focused on the development of specialized aluminum alloys [3,4]. Collaborators from the University of Massachusetts, Dartmouth and the Naval Undersea Warfare Center have reported on performance studies of Al– H_2O_2 semi-fuel cells [5,6].

The use of a magnesium anode in place of the aluminum anode to achieve higher cell potentials and to exclude the use of the sodium hydroxide in the seawater electrolyte, as well as focus on current densities below 50 mA cm^{-2} , has been investigated by Medeiros et al. [7,8]. The microfibre carbon cathode substrates described herein are for use in the acidic Mg– H_2O_2 system. The overall cell reaction for the Mg–SFC in an acidic medium is



Several catalysts have been investigated for use in fuel cells [9]. Many of these catalysts (including palladium and iridium independently) have been incorporated in carbon based pastes [10]. Collman and Kim have reported that iridium porphyrin complexes are very active catalysts [11]. Cox and Jaworski have used a palladium–iridium combination on a glassy carbon microelectrode for the quantitative determination of H_2O_2 [12]. A combination of palladium and iridium has been shown in the NUWC

* Corresponding author. Tel.: +1-508-999-8587; fax: +1-508-999-9167.
E-mail address: rbessette@umassd.edu (R.R. Bessette).

electric propulsion laboratories to improve the electrochemical efficiency for the reduction of H_2O_2 and to improve cell voltage relative to the use of a metallic silver cathode [13].

Hasvold et al. have studied the use of large “bottle brush” catalyzed carbon fiber electrodes in a non-separated Al– H_2O_2 system at the 5 mM level of H_2O_2 [14]. Their success was attributed to an increase in the ratio of cathode to anode area. Because of more stringent system power and volume requirements, our investigations have centered on the use of magnesium anodes and on achieving very large cathode surface area to volume ratios. Achievement of small volume, large surface area cells will permit operation at low H_2O_2 levels and result in

1. reduction in the size of the H_2O_2 storage tank,
2. higher electrochemical reaction efficiencies (less H_2O_2 decomposition), and
3. elimination of the need for a cell separator membrane (negligible direct reaction of catholyte with the anode).

This latter result will bring about greater system simplicity, a modest gain in cell voltage at low rate and a significant increase in cell voltage at high rate.

2. Experimental

All chemicals used in this investigation were of reagent grade quality and were used as obtained from the supplier (Alfa Aesar, Aldrich, and Fisher Scientific) without further purification. All solutions were prepared using glass distilled, deionized water. The sea salt used was ASTM-D 1141-52 (Lake Products), the hydrogen peroxide was 50% grade (Elf Atochem) and the carbon microfibres were pitch based and 10 μm diameter (Mitsubishi Chemical). The fibers were accurately cut to 0.50 mm in length by Engineered Fibers Technology, LLC. The carbon microfibres 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.

The simultaneous deposition of Pd and Ir on the carbon substrate was carried out by cyclic voltammetry from -150 to -300 mV versus Ag–AgCl at a rate of 1.0 mV s^{-1} 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°C and contained 2.0 mM palladium(II) chloride (PdCl_2), 2.0 mM sodium hexachloroiridate (Na_2IrCl_6), 0.2 M KCl, and 0.1 M HCl. The carbon fiber electrode was soaked in 6 M HCl for 15 min and rinsed with distilled water prior to use. A three-electrode cell consisting of the substrate carbon fiber working electrode, a Ag–AgCl reference electrode, and a Pt auxiliary electrode was used for the depositions.

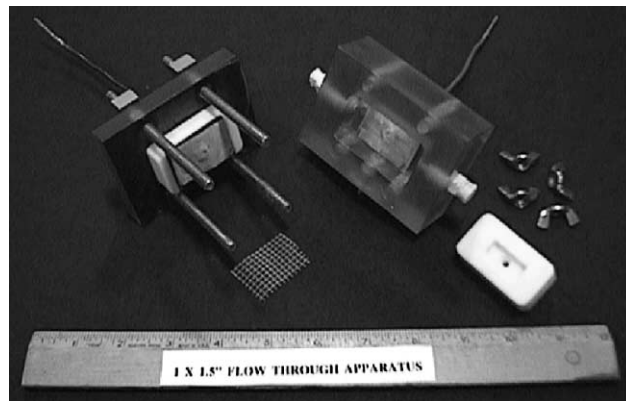


Fig. 1. Flow-through test cell.

Full cell performance was carried out using a $25 \text{ mm} \times 38 \text{ mm}$ ($1'' \times 1.5''$) cell made of polycarbonate (Fig. 1).

A Vexar spacer maintained the cell gap at 0.7 mm. The anode and cathode were mounted on individual current collector bus bars. The two electrodes were mounted vertically and were separated by the Vexar screen spacer. When a Nafion 115 membrane was used, Vexar spacers were used on each side of the 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. 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, peristaltic pumps, a heat exchanging coil in a constant temperature bath to maintain temperature, the flow through cell and a return to the reservoir. Cell current was regulated by means of a multistep load resistance substitution box. Cell current, voltage, inlet and outlet temperatures, and evolved gas flow rate were simultaneously monitored and recorded by the computer data logging system. The software used for the data acquisition was Lab Tech Notebook.

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 nm.

3. Results and discussion

Fabrication of microfibre carbon electrodes (MCEs) using a textile science flocking technique has been studied. To our knowledge use of the flocking technique, which involves application of very high electric fields (40–70 kV), with highly conductive and high surface charge carbon fibres, has

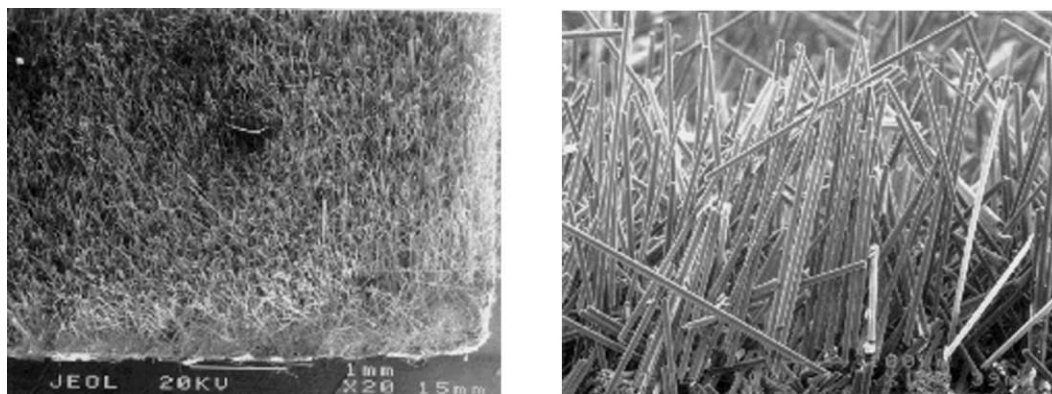


Fig. 2. S.E.M. micrographs of a microfiber carbon electrode. Left: top view at 20 \times . Right: cross-sectional view at 150 \times . Fibres are 0.5 mm long \times 10 μ m diameter.

not been reported upon in the scientific literature. Flocking of the carbon fibers onto a substrate is accomplished by placing the substrate at ground potential and locating the flocking apparatus anode vertically above the substrate at a distance between 170 and 300 mm. A hopper, which contains the fibers to be flocked, is concentric to the anode.

Upon application of the voltage field (typically 70 kV), the fibers are expelled from the hopper toward the substrate. Since the substrate is coated with a conductive epoxy binder, the fibers will be held perpendicular to the surface.

Fig. 2 depicts SEM images showing top and cross sections of a microfibre carbon electrode. This electrode was fabricated using a 250 μ m thick film of conductive epoxy to bind the fibers to the carbon paper substrate.

The conductive epoxy 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 epoxy (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

epoxy on the substrate. A porous carbon paper (0.25 mm thick, Spectracarb) has proven to be an excellent substrate for bonding of the conductive epoxy. In addition, it remains rigid during electrochemical deposition of the Pd–Ir catalyst at 70 $^{\circ}$ C.

Using SEM images, the fiber density of the electrode shown in Fig. 2 was determined to be 55,700 fibers per cm² of electrode geometric area, i.e. the two dimensional area defined by the carbon paper. MCEs having 112,000 fibers per cm² of geometric area have been prepared. The electrode having the latter fiber density has 182 cm² of surface area per cm³ of electrode volume. This electrode volume includes the thickness of the conductive epoxy binder and the carbon paper substrate.

Application of a palladium–iridium catalyst to carbon microfibres with a 100:1 aspect ratio (1.0 mm long, 0.010 mm diameter) was non-uniform. The catalyst was deposited in 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. 3A and B show top views at 100 and 950 \times , respectively, of the 50:1 aspect ratio fibers (0.5 mm long: 0.010 mm diameter) of the

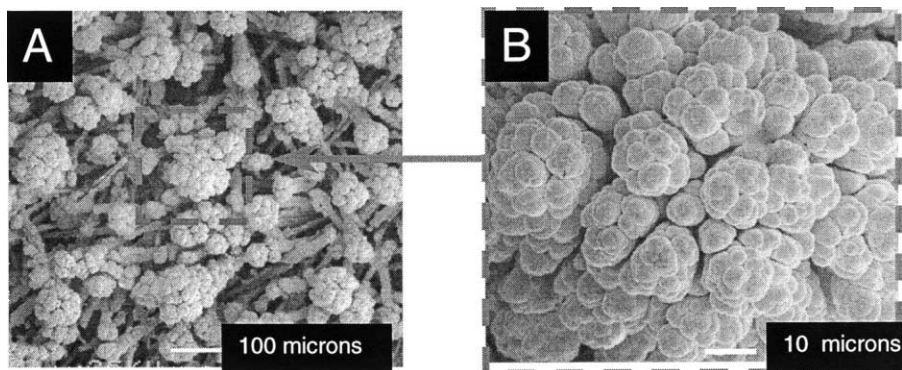


Fig. 3. S.E.M. micrographs of the Pd–Ir catalysed microfiber electrode at 100 \times (3A) and 950 \times (3B). 3B shows the morphology of the Pd–Ir at the center of 3A.

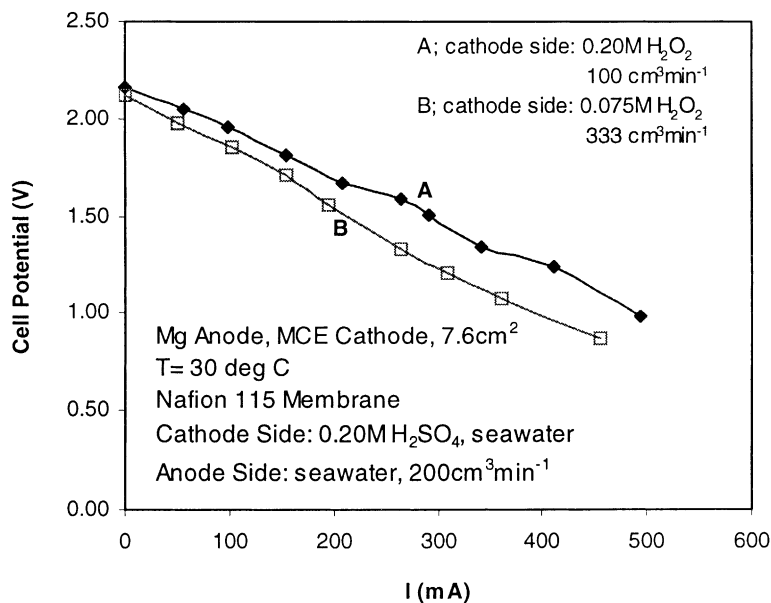


Fig. 4. Performance of the microfiber carbon electrode.

MCE covered with catalyst for the entire length of the fibers. Well formed palladium and iridium clusters are clearly shown. One can conclude that an increase in surface area of several times occurs with the application of the catalyst. For the electrode with 11,200 fibers per cm^2 of geometric area, the total volumetric surface area will be several times — $182 \text{ cm}^2 \text{ per cm}^3$ — of electrode volume. BET determination of the total surface area will be performed to ascertain the increase in surface area with formation of the catalyst clusters.

Magnesium– H_2O_2 cell data show unhindered flow of catholyte through the carbon fiber microelectrode. The full surface area of the catalyzed MCE appears to be accessible. Stability of this catalyst on a carbon surface is excellent. Catalyzed carbon paper substrates have been used repeatedly without any loss of catalyst performance. Curve A of Fig. 4 shows the superior cell voltage to current performance of the MCE in a membrane separated Mg– H_2O_2 cell. The operating conditions for curve A are those established as optimum for a Mg– H_2O_2 cell incorporating a Pd–Ir catalyzed carbon paper cathode. The optimization of the conditions is reported upon by Medeiros et al. [15]. The cell potential of 1.7 V at 190 mA (25 mA cm^{-2}) agrees very favorably with the voltages obtained upon optimizing the operating conditions.

Curve B of Fig. 4 shows the cell voltage to current relationship with a decrease in H_2O_2 concentration to 0.075 M and an associated increase in the catholyte flow rate to $333 \text{ cm}^3 \text{ min}^{-1}$. The slight decrease in voltage of approximately 0.100 V at 25 mA cm^{-2} (190 mA total current) is encouraging in our attempts to significantly lower the concentration of H_2O_2 at which the cell can be operated efficiently.

4. Summary

Microfiber carbon electrodes (MCEs) of significant density have been fabricated using a textile science flocking technique. Volumetric surface area of $182 \text{ cm}^2 \text{ per cm}^3$ has been achieved.

Stable Pd–Ir catalyst cluster formation over most of the carbon fibre surface area is demonstrated. The Pd–Ir catalyst cluster formation is expected to increase the volumetric surface area several fold.

Superior cell voltage to current performance in a Mg– H_2O_2 membrane separated cell has been obtained. Cell voltage at 25 mA cm^{-2} for the cell containing a MCE cathode is similar to the voltage obtained for a cell operating under optimum conditions and employing a Pd–Ir catalyzed carbon paper cathode.

Encouraging cell voltage at the current density of interest, 25 mA cm^{-2} , has been attained for a reduction in the H_2O_2 concentration to 0.075 M.

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References

- [1] D. Linden, Handbook of Batteries, 2nd Edition, McGraw-Hill, New York, 1995.
- [2] A.J. Bard, R. Parsons, J. Jordan, Standard Potentials in Aqueous Solution, IUPAC, Marcel Dekker, Inc. 1985.
- [3] G. Scamans, J. Hunter, C. Tuck, R. Hamlen, N. Fitzpatrick, in: Keily, Baxter (Eds.), Further Development of Aluminum Batteries, Power Sources XII, 1988, p. 363.
- [4] J. Hunter, et al., Aluminum Batteries, European Patent Application no. 0354752, Alcan International, Ltd., 1989.
- [5] R. Bessette, E. Dow, G. Seebach, C. Marsh-Orndorff, H. Meunier, J. Van Zee, M. Medeiros, Enhanced Electrochemical Performance in the Development of the Aluminum–Hydrogen Peroxide Semi-Fuel Cell, *J. Power Sources* 65 (1997) 207.
- [6] R. Bessette, J. Cichon, D. Dischert, Performance optimization of aluminum solution phase catholyte semi-fuel cell, in: Proceedings of the 38th Power Sources Conference, Cherry Hill, NJ, 1998.
- [7] M. Medeiros, E. Dow, R. Bessette, Magnesium-solution phase catholyte in an acid/seawater electrolyte semi fuel cell system, in: Proceedings of the Joint International Meeting of the Electrochemical Society and the Electrochemical Society of Japan, Honolulu, Hawaii, 1999, pp. 17–22.
- [8] M. Medeiros, E. Dow, Magnesium-solution phase catholyte seawater electrochemical system, *J. Power Sources* 80 (1999) 78–82.
- [9] M. Poirier, C. Perreault, L. Couture, C. Sapundzhiev, Evaluation of catalysts for the decomposition of methane to hydrogen for fuel cell applications, in: Proceedings of the First International Symposium on New Materials for Fuel Cell Systems, Montreal, Quebec, Canada, 1995, p. 258.
- [10] T. Okamoto, I. Baba, H. Kato, Japan Patent JP6-36784, Collector for Fuel Cell and Fuel Cell with the Collector, 1992.
- [11] J. Collman, K. Kim, Electrocatalytic four-electron reduction of dioxygen by iridium porphyrins adsorbed on graphite, *J. Am. Chem. Soc.* 108 (24) (1986) 7847.
- [12] J. Cox, R. Jaworski, Voltammetric reduction and determination of hydrogen peroxide at an electrode modified with a film containing palladium and iridium, *Anal. Chem.* 61 (1989) 2176.
- [13] J. Cichon, R. Bessette, D. Dischert, Electrode surface modification for cathode catalysis in semi-fuel cells, in: Proceedings of the 194th Electrochemical Society Meeting, Boston, MA, 1998.
- [14] O. Hasvold, K.H. Johansen, O. Mollestad, S. Forseth, N. Storkersen, The alkaline aluminum–hydrogen peroxide power source in the Hugin II unmanned underwater vehicle, *J. Power Sources* 80 (1999) 254.
- [15] M.G. Medeiros, R.R. Descheres, C.M. Desehenes, D.W. Atwater, Optimization of the Magnesium-Solution Phase Catholyte Semi-Fuel Cell for Long Duration Testing, in: Proceedings of the 22nd International Power Sources Symposium, Manchester, England, 2001.