

# Magnesium-solution phase catholyte semi-fuel cell for undersea vehicles

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## Abstract

A magnesium-solution phase catholyte semi-fuel cell (SFC) is under development at the Naval Undersea Warfare Center (NUWC) as an energetic electrochemical system for low rate, long endurance undersea vehicle applications. This electrochemical system consists of a magnesium anode, a sodium chloride anolyte, a conductive membrane, a catalyzed carbon current collector, and a catholyte of sodium chloride, sulfuric acid and hydrogen peroxide.

Bipolar electrode fabrication to minimize cell stack volume, long duration testing, and scale-up of electrodes from 77 to 1000 cm<sup>2</sup> have been the objectives of this project. Single cell and multi-cell testing at the 77 cm<sup>2</sup> configuration have been utilized to optimize all testing parameters including start-up conditions, flow rates, temperatures, and electrolyte concentrations while maintaining high voltages and efficiencies. The fabrication and testing of bipolar electrodes and operating parameter optimization for large electrode area cells will be presented. Designs for 1000 cm<sup>2</sup> electrodes, electrolyte flow patterns and current/voltage distribution across these large area cells will also be discussed.

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## 1. Introduction

Primary batteries employing aqueous electrolytes [1,2] have been under development by the US and other countries [3], both government and commercial, since the 1940s. Emphasis has been placed on aluminum [4–6] and magnesium anodes [7] due to their high faradaic capacity, low atomic weight and high standard potentials. Of particular interest is their use in undersea vehicles due to the availability of seawater to act as an electrolyte or electrolyte solvent, further enhancing their effectiveness as an energy source on a systems basis.

A semi-fuel cell (SFC) consists of a metallic anode that is consumed by a conventional oxidation reaction, and a soluble chemical species that is metered into the cell and is electrochemically reduced at the cathode surface. This blends characteristics of conventional batteries and fuel cells, hence the name “semi-fuel cell” or SFC.

Since the soluble solution phase catholyte species reacts directly with the anode producing no useful energy, a con-

ductive membrane must be used to separate the two flowing electrolytes, anolyte and catholyte.

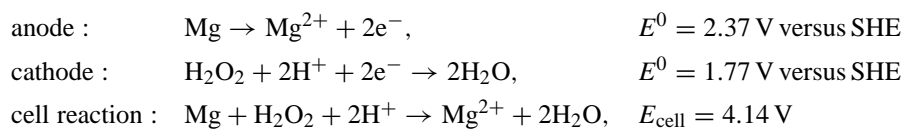
Electrolyte species are carried in concentrated form in separate tankage and metered into the flowing electrolyte as needed. The cell stack of the SFC is a series of bipolar plates. Each bipolar plate is composed of the anode material, a conductive adhesive, and a catalyzed substrate cathode material.

Development of affordable, long endurance semi-fuel cell technology to meet the demands of current and future unmanned underwater vehicles (UUVs) is a major technical challenge. The magnesium–hydrogen peroxide electrochemical couple [8,9] has a theoretical cell potential of 4.14 V which is higher than the present energy sources, aluminum–silver oxide (Al–AgO) [10] or aluminum–hydrogen peroxide (Al–H<sub>2</sub>O<sub>2</sub>) [11,12]. In addition, the Mg–H<sub>2</sub>O<sub>2</sub> system is lighter in weight, environmentally friendly and less expensive. This new solution phase system should be capable of performing as a high energy density source for low power, long endurance UUV applications.

The theoretical half-cell and overall cell voltages for the magnesium–hydrogen peroxide semi-fuel cell system [13,14] are as follows:

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The specific challenges addressed by this paper include the evaluation of membrane types and treatments, fabrication and testing of bipolar electrodes, and automated delivery control of reactants in a Mg-SFC system.

## 2. Experimental section

Materials used included: sodium chloride (ACS grade, Spectrum Chemical), hydrogen peroxide (50% CG-grade, Elf Atochem), palladium chloride (ACS grade, Alfa Aesar), sodium hexachloroiridate (ACS grade, Alfa Aesar) and sulfuric acid (ACS grade, 96%, Aldrich Chemicals). The magnesium alloy used was AZ61. The carbon microfibers, obtained from Mitsubishi Chemical, were pitch-based and 10  $\mu\text{m}$  in diameter. The 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. Conductive carbon ink, from Creative Materials Inc., was used to adhere the fibers to the substrate.

Each test was performed for a minimum of 4 h to a maximum of 60 h using a flowing electrolyte apparatus and a cell fixture. The flowing electrolyte apparatus contains two electrolyte tanks and two flow loops. One tank contained the anolyte that was pumped to the magnesium anode side and the second electrolyte tank contained the catholyte that was pumped to the cathode side. The cell fixture could accommodate up to five 77  $\text{cm}^2$  bipolar electrodes. The cell was assembled as follows: a magnesium anode was fixed to an end plate, a mechanical separator (Vexar) was added next, followed by a membrane, a second mechanical separator and finally an electrocatalyst adhered to an end plate.

A high surface area cathode has recently been developed for the Mg–H<sub>2</sub>O<sub>2</sub> SFC. It is fabricated using a novel method described in [15]. Briefly, the fabrication of the cathode utilizes an electrostatic flocking process. The flocking technique is used to apply carbon fibers to a current collector such that the fibers are oriented normal to the surface of the substrate. The process generally involves charging the fibers of interest in an electric field. The electric field then accelerates the fibers toward the electrode of opposite charge (i.e. the substrate). The fibers become embedded in an adhesive that is spread on the surface of the substrate prior to applying the electric field.

The final step is curing of the adhesive to anchor the fibers to the current collector. A Pd/Ir alloy is then deposited on the microfibers to facilitate the reduction of the hydrogen peroxide. When the electrode is placed in the cell, the catalyzed fibers penetrate into the catholyte flow stream.

The performance of the magnesium–hydrogen peroxide semi-fuel cell is principally dependent on five parameters: the H<sub>2</sub>O<sub>2</sub> catholyte concentration, the electrolyte temperature, the catholyte flow rate, the anolyte flow rate and the current density. A Taguchi method [16] multi-variable array was utilized to maximize the performance and minimize the number of tests in an effort to optimize these parameters of the Mg–H<sub>2</sub>O<sub>2</sub> system. A summary of these data is described in [17].

## 3. Results

Mg-SFC tests have focused on investigating several different ionically conductive membranes and start-up conditions. The membranes included Nafion 112 and 115 manufactured by Dupont; M-03596 and M-03597 from W.L. Gore and FAS 7.5 fabricated by Advanced Membrane Systems. The Dupont and Gore membranes are both proton exchange membranes whereas the FAS membrane is a microporous type membrane.

When the FAS and Gore membranes were tested in the Mg-SFC, their performance was found to be less satisfactory than that obtained with the Nafion membrane. The attraction of the FAS and Gore membranes was the ability to test these membranes in a dry state. No treatment was necessary for conductivity to take place, nor was wettability a problem with these membranes during start-up.

The Nafion membranes have been the membranes of record for all the optimization and characterization of the Mg-SFC system. The manufacturer suggests soaking and or treating these membranes prior to use. Several procedures were evaluated for the treatment of Nafion membranes [18–20]. These procedures included (1) soaking in seawater for a minimum of 12 h and tested wet; (2) soaking in acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HCl) both at room temperature and elevated temperatures for a fixed time followed by water rinsing at room temperature and elevated temperatures; (3) boiling in dilute H<sub>2</sub>O<sub>2</sub> solution, rinsing in boiling water, boiling in dilute H<sub>2</sub>SO<sub>4</sub> solution, and rinsing in boiling water. An additional procedure developed at NUWC involves treating the membrane in glycerin and testing the membrane in dry state after the treatment. This procedure, for which a patent application has been submitted [21], results in rapid start-up and repeatable cell performance. Treating the Nafion membrane in boiled acid as described in [18] also has the advantage of testing the membrane in a dry state. Fig. 1 compares the cell performance for Nafion membranes treated in glycerin, in seawater, boiled in acid and in an acid/hydrogen peroxide combination.

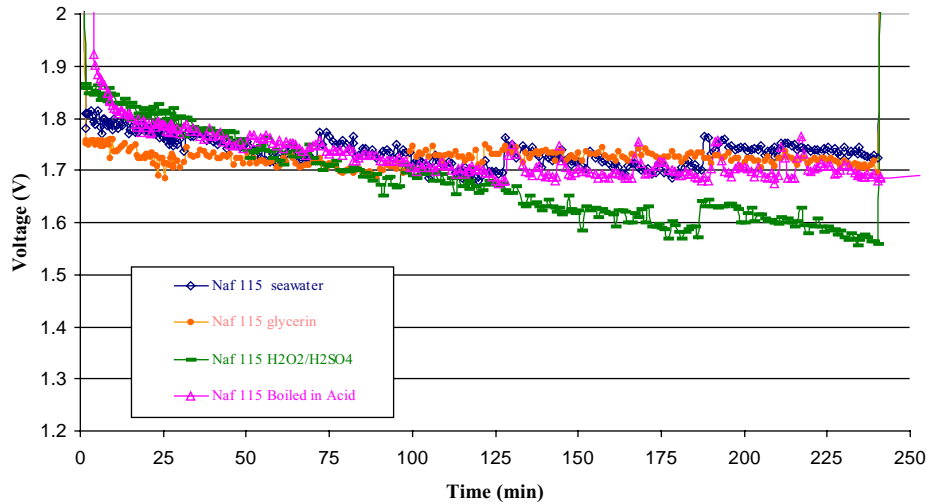


Fig. 1. Cell voltage profiles for different Nafion treated membranes.

As Fig. 1 depicts, the cell voltages observed for the glycerin, the boiled in acid and the seawater soaked membranes were equivalent. These voltages (1.7–1.8 V) were steady with time up to 240 min. The acid/hydrogen peroxide treated membrane resulted in lower cell voltage after 125 min compared to the other membranes for the same discharge time. Although, the seawater soaked membrane showed high and consistent voltages; it was not selected for further testing due to the fact that it had to be kept hydrated prior to testing.

Mg-SFC tests with boiled in acid and glycerin treated membranes maintained voltages above 1.7 V at  $25 \text{ mA cm}^{-2}$  for 4 h with magnesium and hydrogen peroxide efficiencies ranging from 77 to 86%. The specific energies for the Mg-SFCs with boiled in acid treated membranes ranged from 400 to  $430 \text{ Wh kg}^{-1}$  while a range of

$500\text{--}520 \text{ Wh kg}^{-1}$  was obtained for the Mg-SFCs with the glycerin treated membranes. The specific energy values are based on the weights consumed during discharge of the magnesium anode, hydrogen peroxide and acid.

A long duration (30 h) discharge with a dry glycerin treated Nafion 115 membrane was conducted to evaluate the membrane with time and to validate the LabView-based automated control system. This control system provides  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  infusion into the catholyte flow stream. The acid is controlled by the output signal of a pH sensor located in the catholyte flow loop, and the  $\text{H}_2\text{O}_2$  control uses the cell voltage as a feedback signal. Fig. 2 below depicts this discharge profile; it shows excellent voltage stability for the entire discharge time with cell voltages between 1.80 and 1.77 V. Once the automated control system and the long duration performance of the treated membrane was

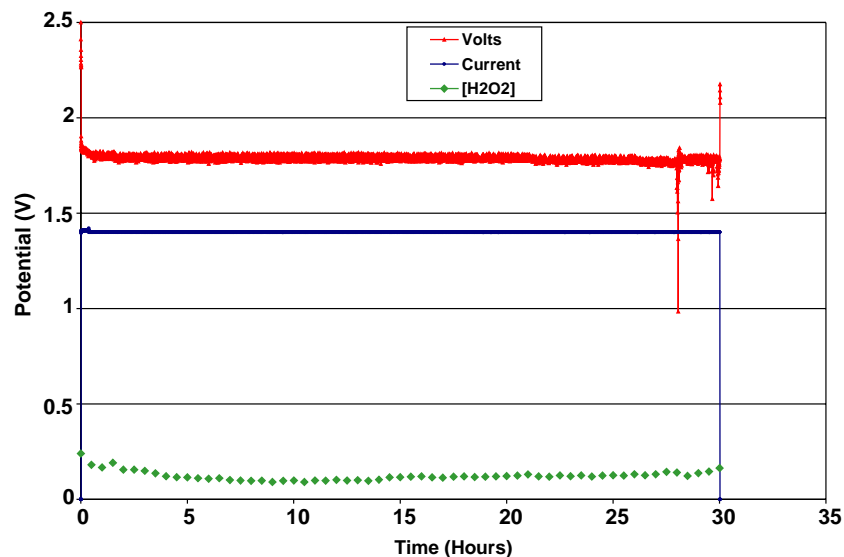


Fig. 2. Thirty-hour discharge profile with dry Nafion membrane; glycerin treated.

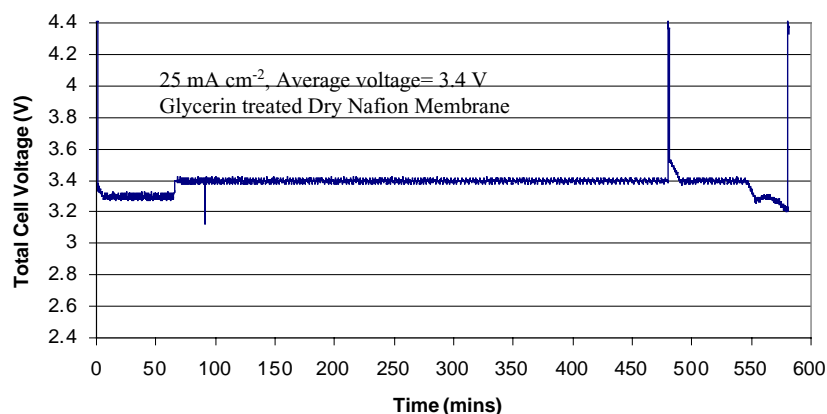


Fig. 3. Bipolar two-cell discharge profile.

validated, the next step was to conduct bipolar multi-cell long duration discharges.

Bipolar inserts were fabricated to accept bipolar electrodes. The insert contains inlets and outlets for the dual flow electrolytes and flow channels for the proper distribution of the electrolytes over the entire surface of the electrodes. Once adhesion of the magnesium anode to the substrate of the Pd/Ir catalyzed cathode was accomplished and tested, this bipolar electrode was then adhered to the insert. A two-cell bipolar stack consists of a magnesium anode end plate, a mechanical separator, a Nafion membrane, a mechanical separator, a bipolar electrode insert, a mechanical separator, a second membrane, a mechanical separator and a Pd/Ir catalyzed cathode end plate (Fig. 5).

Fig. 3 illustrates the discharge profile for a two-cell bipolar test utilizing dry glycerin treated membranes.

The experiment ran for 8 h, then the cell was shut down and drained of electrolyte. After recharging with electrolyte the cell was re-started the following day and continued for another 3 h. This two cell bipolar system demonstrated excellent re-start ability and points to the possibility of developing a multi-use system. Total two cell voltage of 3.4 V was observed for the duration of the test. The experiment was stopped due to electrolyte crossover across gasket seals. This problem has been addressed and is explained in the flow frame description paragraphs that follow.

The Mg-SFC system concept is pictured in Fig. 4. The reactants will be housed in bladders that reside within containers. The injection of reactants will be controlled by the duty cycle on the solenoid valves from each bladder. The anolyte and catholyte flow loops will be linked by a crossover valve in order to provide fluid to fill the volume around the acid bladder. The crossover valve will be slaved to the acid injection valve to minimize cross flow between the loops. The anolyte flow loop will have a small flow into and out of the acid bladder container. This will allow anode reaction products to settle out in the quiescent volume around the bladder.

The operation of the system is controlled by two feedback loops. First, the acid injection is controlled by the output signal of a pH sensor in the catholyte flow loop. The control

method is to allow the pH to vary between two set points. When the pH gets too high, the solenoid valve is opened and acid enters the flow loop. When the pH falls below the lower bound, the solenoid valve is closed. The hydrogen peroxide injection method uses the voltage of the cell as the feedback signal. When voltage is high, peroxide injection is stopped. When the voltage falls below the lower bound, the injection flow is turned on. This method was demonstrated in a 30 h test (Fig. 2) and provided extremely stable system control for the duration of the test. This method has been used for all tests that followed the 30 h test and has demonstrated its control and stability time after time.

The most recent focus has been on the fabrication and testing of the 1000 cm<sup>2</sup> electrodes and the flow frames to support the bipolar electrodes. The flow frame (Fig. 5) serves the purpose of holding the electrode, distributing electrolyte across the electrolyte face and reducing leakage currents between cells. Grooves on each face of the flow frame carry the electrolyte over each face of the bipolar electrode. The electrolyte follows through a long path around the electrode to maximize the resistance in the leakage current path to

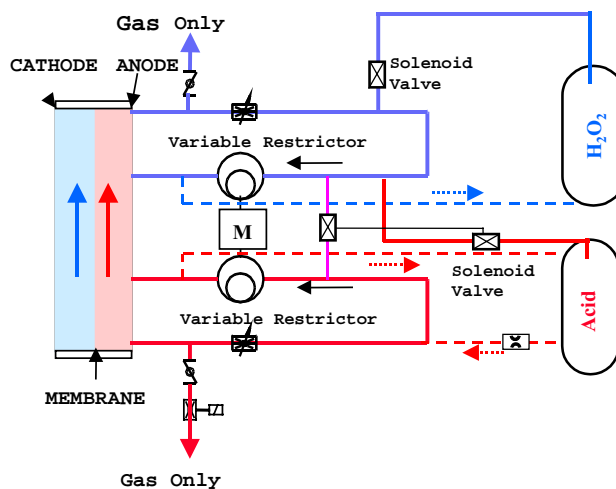


Fig. 4. Mg-SFC concept system.

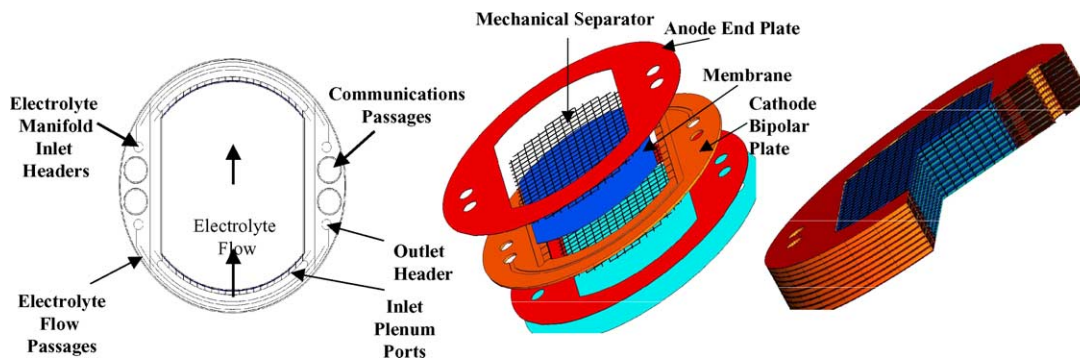


Fig. 5. Flow frame concepts: single, bipolar and stack.

adjacent cells. A relatively large inlet plenum with many small slots into the electrode assures even flow distribution across the cell. The electrode is recessed into the flow frame deep enough to avoid blocking the small slots. Tests with this design were successful, but it proved very difficult to prevent one electrolyte from leaking over to the other side.

The front and backsides of the frame are identical in pattern, resulting in places where the grooves face each other across a gasket seal. The gasket seal can deflect at the inlet and outlet ports and forms an electrolyte leakage path to the other side. To resolve this problem, a very thin fiberglass sheet was adhered to the faces of the frames to close the electrolyte channels and provide positive clamping of the gasket. This solved most of the leakage problems. The final leakage problem comes from manufacturing tolerances on thickness and surface flatness. One must be careful to keep the flow frame flat and uniform.

The thin fiberglass layer increased the thickness of the electrolyte gap over the electrode. It has been shown that the cathode performance is flow rate dependent. However, the pumping energy cost to double the flow of the electrolyte over the electrode exceeds the voltage improvement achieved. An alternate way to increase the flow over the electrode is to reduce the thickness of the flow path without changing the volumetric flow rate. The pumping energy cost is very low and this allows a significant reduction in the catholyte concentration needed to achieve a given voltage output. To that end, the flow frames were revised to eliminate the small grooves to reduce the overall thickness so that the electrode was flush with the surface of the frame. Small slots were then cut into the thin fiberglass sheet to provide electrolyte flow passages across the electrode. Experiments showed 1.7 V per cell could be maintained with almost a threefold reduction in hydrogen peroxide concentration.

#### 4. Summary

A magnesium–hydrogen peroxide semi-fuel cell continues to be investigated at the Naval Undersea Warfare Center (NUWC) for the propulsion of underwater vehicles. Recent focus and the topic of this paper has been on start-up issues,

membrane treatments, fabrication of bipolar electrodes and scaling of the electrodes from 77 to 1000 cm<sup>2</sup>.

A new method for the treatment of Nafion membranes was developed and successfully demonstrated. This method also addresses start-up issues; the Nafion membranes can be used in a dry state with instantaneous results. The fabrication of bipolar electrodes was accomplished and tested. Bipolar electrode flow frames were manufactured and optimized to reduce leakage currents and maintain high voltages with low reactant concentrations. Finally, a system concept was introduced where a two loop operation is discussed and the operation of an automated management and control system was demonstrated.

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