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Optimization of the magnesium-solution phase catholyte semi-fuel cell for long duration testing

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Abstract

A magnesium semi-fuel cell (Mg-SFC) was investigated as an energetic electrochemical system for low rate, long endurance undersea vehicle applications. This electrochemical system uses a Mg anode, a sea water electrolyte, a Nafion membrane, a carbon paper cathode catalyzed with Pd and Ir, and a catholyte of hydrogen peroxide in a sea water/acid electrolyte. Unique to the approach described here is the use of a magnesium anode together with the introduction of the catholyte in solution with the sea water, thus operating as a semi-fuel cell as opposed to a battery. Five critical operating parameters were optimized using a Taguchi matrix experimental design. Using these optimized conditions, high voltage and high efficiencies were obtained during long duration tests.

Keywords: Magnesium anodes; Semi-fuel cells; Hydrogen peroxide; Taguchi matrix

1. Introduction

Primary batteries employing aqueous electrolytes [1,2] have been under development by the USA 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 application for undersea vehicles due to the availability of sea water to act as an electrolyte or electrolyte solution; further enhancing their effectiveness as an energy source on a systems basis.

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_2O_2) [11–13]. In addition, the Mg–H_2O_2 system is lighter in weight, environmental-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 [14,15] are the following.

Anode	$Mg \rightarrow Mg^{2+} + 2e^-$	$E^0 = 2.37$ V vs. SHE
Cathode	$H_2O_2 + 2H^+ + 2e^- \rightarrow 3H_2O$	$E^0 = 1.77$ V vs. SHE
Cell reaction	$Mg + H_2O_2 + 2H^+ \rightarrow Mg^{2+} + 2H_2O$	$E_{cell} = 3.58$ V

The performance of the magnesium–hydrogen peroxide semi-fuel cell is principally dependent on five parameters: (1) the H_2O_2 catholyte concentration; (2) the electrolyte temperature; (3) the catholyte flow rate; (4) the electrolyte flow rate and (5) the current density. With all these variables in mind, determination of the maximum performance and efficiency would require an unacceptably large number of tests by the conventional method of changing one variable at a time while keeping all others constant. However, a Taguchi method [16] multi-variable array was utilized to maximize the data collection and minimize the number of tests.

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Measuring the effects of changing these variables one at a time while holding the rest constant (conventional experimental approach) would require 243 tests (3^5 or five parameters at three levels for each parameter). Through the use of orthogonal arrays via the Taguchi method, the number of tests was reduced to only 18 for the magnesium–hydrogen peroxide system.

2. Experimental

Chemicals used included: sea salt (ASTM-D 1141-52, Lake Products), hydrogen peroxide (50% CG-grade, Elf Atochem), and sulfuric acid (ACS grade, 96%, Aldrich Chemicals).

Each test was performed over a 4 h time period using the apparatus pictured in Fig. 1. This ensured a fair length of time to judge the validity of the test. The flowing electrolyte apparatus contained two electrolyte tanks and two flow loops. One tank contained the sea water electrolyte that was pumped to the magnesium anode. The second electrolyte tank contained sea water, hydrogen peroxide and acid; this electrolyte was pumped to the cathode side of the cell. The cell fixture used could accommodate a separator/membrane in the cell, thus separating the anode reaction from the cathode side.

The five parameters and the three levels for each parameter are summarized in Table 1. Application of the Taguchi method is accomplished by adjusting each parameter concurrently throughout the formulated matrix in an equal number of times. For any pair of columns, all combinations of parameter levels occur an equal number of times. Once data had been collected an error analysis was performed on each individual test. Table 2 summarizes the 18 experiments devised by the Taguchi matrix.

3. Results

Once the test matrices were completed, a function η based on the signal to noise ratio was determined. This value of η was determined by the following equation.

$$\eta = -10\log_{10}(\text{mean square reciprocal quality characteristic})$$

$$\eta = -10\log_{10}\left[\frac{1}{\mu^2}1 + 3\left(\frac{\sigma^2}{\mu^2}\right)\right]$$

Fig. 1. The dual-flow electrolyte apparatus.

where μ is specific energy density (Wh kg^{-1}), total energy produced divided by the total mass of energetic materials consumed (anode material and catholyte). σ is standard error of μ. A unique η value is calculated for each specific test (η_i). A new overall average η (η_0) value for a specific parameter is then calculated by averaging the η_i values of all tests that contain the parameter.

Fig. 2 is a plot of all the η (signal to noise ratio dependent) values for the magnesium–hydrogen peroxide semi-fuel cell matrix tests. Each η value is based on the average of six individual tests, which contain that parameter. The optimum value of each of the variables is determined by the largest η value as compared to the other members of the group. The values used for the optimum conditions test were chosen by interpreting the data from this figure.

As a result, it was concluded that for maximum specific energy, the optimum conditions are as follows:

- flow rate, anode: 200 cm^3 min^{-1};
- flow rate, cathode: 100 cm^3 min^{-1};
- H_2O_2 concentration: 0.20 M;
- current density: 25 mA cm^{-2};
- temperature: 25°C.

Under these optimum conditions, a single-cell Mg-SFC (77 cm^2) test was conducted and the voltage, current, power versus time results are pictured in Fig. 3. Utilizing the optimum conditions resulted in $\eta = 59.8$. Anodic and cathodic efficiencies of 80 and 60% were achieved, respectively.

Table 1
Mg–H_2O_2 test parameters

$[H_2O_2]$ (M)	Temperature (°C)	Catholyte flow rate (cm^3 min^{-1})	Electrolyte flow rate (cm^3 min^{-1})	Current density (mA cm^{-2})
0.20	0.0	25.0	25.0	10.0
0.30	25.0	100.0	100.0	25.0
0.40	50.0	200.0	200.0	50.0

Table 2
Eighteen experiments of the Taguchi matrix

Test No.	Flow rate, anode ($cm^3\ min^{-1}$)	Flow rate, cathode ($cm^3\ min^{-1}$)	$[H_2O_2]$ (M)	$[H_2SO_4]$ (M)	Current density ($mA\ cm^{-2}$)	Temperature (°C)
1	25	25	0.4	0.01	10	0
2	25	100	0.2	0.05	25	25
3	25	200	0.3	0.1	50	50
4	100	25	0.4	0.05	25	50
5	100	100	0.2	0.1	50	0
6	100	200	0.3	0.01	10	25
7	200	25	0.2	0.01	50	25
8	200	100	0.3	0.05	10	50
9	200	200	0.4	0.1	25	0
10	25	25	0.3	0.1	25	25
11	25	100	0.4	0.01	50	50
12	25	200	0.2	0.05	10	0
13	100	25	0.2	0.1	10	50
14	100	100	0.3	0.01	25	0
15	100	200	0.4	0.05	50	25
16	200	25	0.3	0.05	50	0
17	200	100	0.4	0.1	10	25
18	200	200	0.2	0.01	25	50

Following the optimization of the parameters for the Mg–H_2O_2 system, several experiments were conducted to determine catalyst stability with time along with the start/restart capabilities. Experiments were conducted for 8 h, utilizing the optimum conditions. At the end of the 8 h; the magnesium anode was replaced (due to thickness limitations) and the experiment was restarted and continued for another 8 h. This was conducted for five experiments, the last experiment utilized 'real' versus synthetic sea water purchased from Lake Products. No differences in voltage or performance efficiency were evident between the 'real' and the synthetic sea water. Fig. 4 illustrates the five experiments, the start/restart performance and the anodic and cathodic efficiencies associated with each experiment. It is evident from Fig. 4 that the system recovers well and maintains its voltage with time. The second experiment shows a voltage decrease from the normal 1.7–1.8 V to a voltage decay below 1.5 V. This was attributed to a contact problem between the magnesium anode and the current collector, as was evident once the cell was taken apart after 5 h under load.

4. Summary

Demonstrated was the effective use of the Taguchi method to determine the optimum conditions for the magnesium–hydrogen peroxide semi-fuel cell system in a reasonable time frame with a minimum number of tests.

The magnesium–hydrogen peroxide system had an η value ranging from (based on signal to noise ratio) 52.5 to 57.9 over all of the Taguchi orthogonal array tests

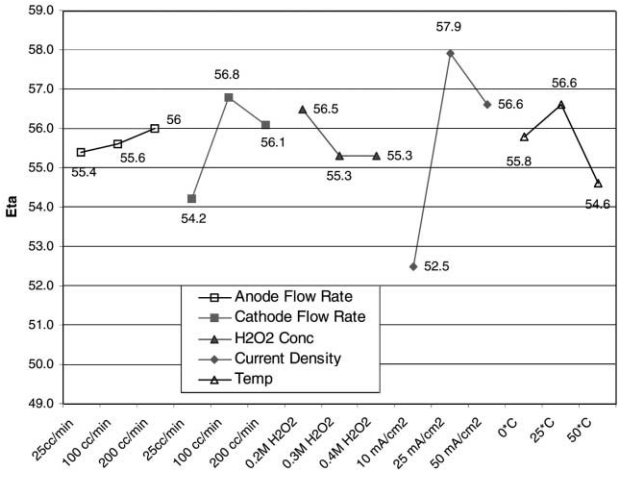

Fig. 2. Summary of the Taguchi matrix.

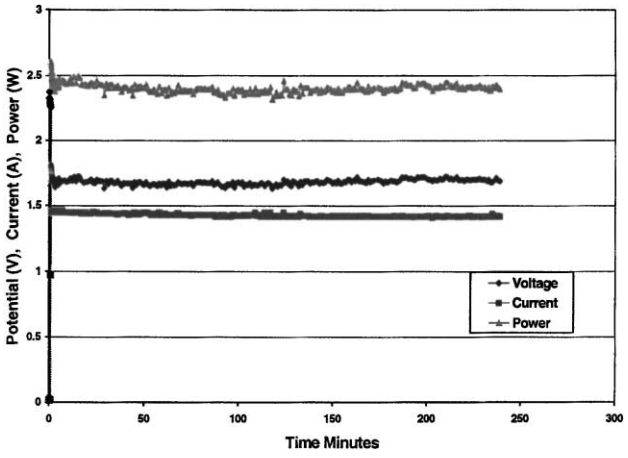

Fig. 3. Optimum Taguchi test.

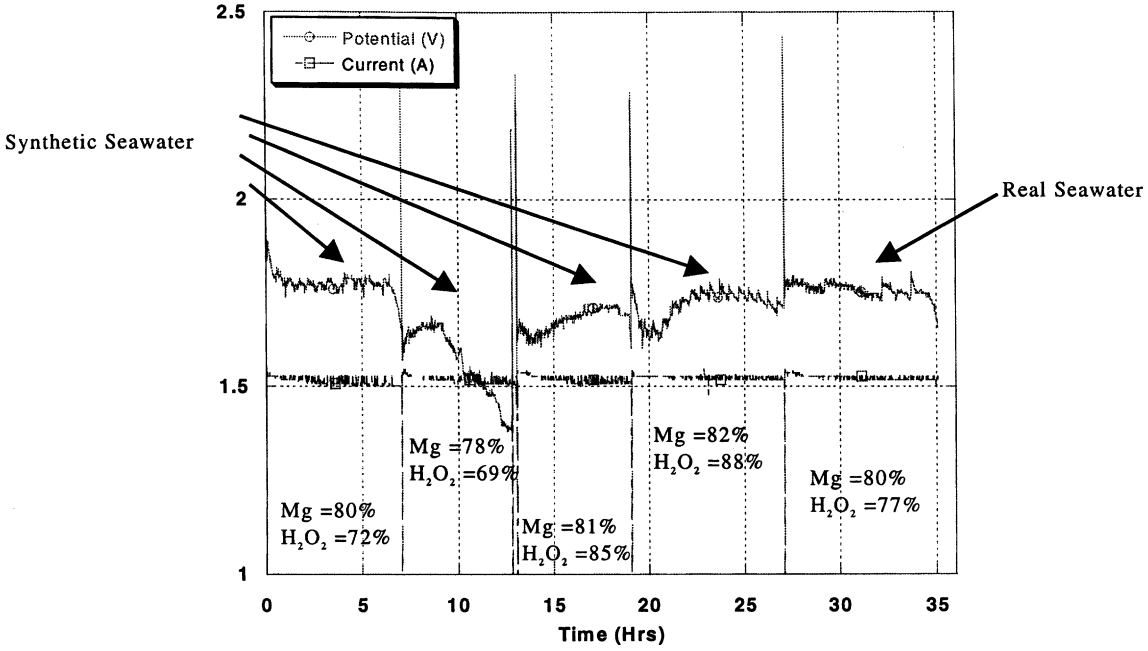

Fig. 4. Start/restart experiments.

performed. The test performed with all the optimum conditions resulted in an η value of 59.8; clearly the Taguchi Method predicted optimum conditions which yielded the best performance.

The optimum test conditions for the magnesium–hydrogen peroxide system are:

- flow rate, anode: 200 cm^3 min^{-1};
- flow rate, cathode: 100 cm^3 min^{-1};
- H_2O_2 concentration: 0.20 M;
- current density: 25 mA cm^{-2};
- temperature: 25°C.

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