Magnesium-solution phase catholyte seawater electrochemical system

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Abstract

A magnesium-solution phase catholyte semi-fuel cell (Mg-SFC) system was investigated as an energetic electrochemical system for low rate, long endurance undersea vehicle applications. This electrochemical system consisted of a magnesium anode and a solution phase catholyte of hydrogen peroxide or hypochlorite, in a seawater electrolyte. Polarization profiles of the Mg-SFC were performed to determine the corresponding voltages at applied current densities ranging from 10 to 50 mA cm^{-2}. Voltages of 1.0 V to 1.8 V were observed at these current densities. Constant current-density tests at 25 mA cm^{-2} for 60 min were also performed to determine voltage stability with time. These tests showed voltages of 1.3 V when a magnesium anode and an electrocatalyst of nickel foil catalyzed with palladium and iridium were utilized. When an electrocatalyst of planar carbon catalyzed with palladium and iridium was tested, the corresponding voltage was 1.5 V. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Primary batteries employing aqueous electrolytes [1] have been under development by the US Navy and other countries, both government and commercial, since the 1940s.

Emphasis has been placed on aluminium [2] and magnesium [3] anodes due to their high faradaic capacity, low atomic weight and high standard potentials [4]. Of particular interest is their application for undersea vehicles due to the availability of seawater to act as an electrolyte or electrolyte solution, further enhancing their effectiveness as an energy source on a systems basis.

Magnesium/cuprous chloride [1] and magnesium/silver chloride [5] were the front runners; eventually they were replaced with lower-cost alternative cathodes such as lead chloride and manganese dioxide; but all had equally low specific energies.

Developments of higher specific energy systems included replacing magnesium with aluminium [6,7] and using silver oxide as the cathode [8]. This enabled exceptional specific power and energies but with increased costs. To reduce the cost without compromising specific energy, the expensive silver oxide cathodes were replaced with solution phase catholytes, such as hydrogen peroxide [9] or sodium hypochlorite. These results are extremely promising by virtue of the reduced cost of materials while achieving specific energies upwards of 200 W h kg^{-1} at current densities of 100–1200 mA cm^{-2}.

Additional developments on a solution phase catholyte for aluminium aqueous batteries at reduced current densities indicated specific energies upwards of 400 W h kg^{-1}, utilizing sodium hydroxide mixed with seawater as a caustic electrolyte. Other countries, notably in Scandinavia [10,11], have successfully employed magnesium-seawater batteries whereby the cathode consists of oxygen saturated in the seawater electrolyte which is reduced on a catalytic surface opposite the magnesium anode. This is highly efficient on a systems basis due to the fact that there is no sodium hydroxide required, greatly reducing the system weight. However, the lower reduction potential for oxygen over hydrogen peroxide and also the flow-rate to surface-area constraints make these systems impractical for vehicle use.

Other magnesium-seawater batteries [10] have been developed, all of which include solid electrodes, including silver chloride, cuprous chloride, lead chloride, cuprous iodide, cuprous thiocyanate and manganese dioxide. Unique to NUWC's approach is the use of the magnesium anode together with the introduction of the cathode as a liquid in solution with the seawater, thus operating as a semi-fuel cell as opposed to a battery.
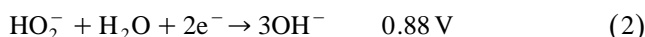
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This effort is similar to the previous work by virtue of the commonality of the solution phase catholytes (hydrogen peroxide (H_2O_2) [12–14] and sodium hypochlorite (NaOCl) [15–17], but different from the previous work by virtue of the magnesium anode in place of the aluminium anode. In addition, this system will exclude the use of the sodium hydroxide in the seawater electrolyte; as well as focus on current densities below 50 mA cm^{-2}.

Preliminary calculations indicate that the elimination of the sodium hydroxide electrolyte and activation of the anode in pure seawater will enable an increase in specific energy of 50%, thus 550 W h kg^{-1}, or six times that of silver–zinc. As a simpler system, an increase in reliability and a reduction in cost will also be realized.
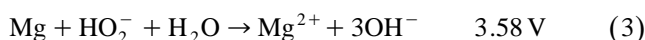
The approach was to characterize the electrochemical and chemical phenomena occurring at the electrodes. The redox potentials [18] vs. SHE associated with the magnesium–hydrogen peroxide (Mg–H_2O_2) system are:Anode:

$$Mg \rightarrow Mg^{2+} + 2e^- \qquad 2.70\,V \qquad (1)$$

Cathode:

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \qquad 0.88\,V \qquad (2)$$

Cell Reaction:

$$Mg + HO_2^- + H_2O \rightarrow Mg^{2+} + 3OH^- \qquad 3.58\,V \qquad (3)$$
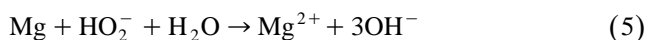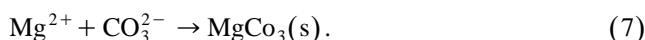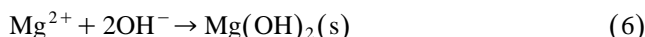
Unfortunately, these theoretical open circuit potentials are reduced and the electrochemical performance inhibited by the following parasitic reactions:Decomposition reaction:
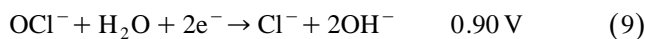
$$2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow \qquad (4)$$

Direct reaction:

$$Mg + HO_2^- + H_2O \rightarrow Mg^{2+} + 3OH^- \qquad (5)$$

Precipitation reactions:

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

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCo_3(s). \qquad (7)$$

The redox potentials [17] vs. SHE associated with the magnesium–hypochlorite system (Mg–OCl$^-$) are:Anode

$$Mg \rightarrow Mg^{2+} + 2e^- \qquad 2.70\,V \qquad (8)$$

Cathode:

$$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \qquad 0.90\,V \qquad (9)$$

Cell reaction:

$$Mg + OCl^- + H_2O \rightarrow Mg^{2+} + Cl^- + 3OH^- \qquad 3.60\,V \qquad (10)$$

Decomposition reaction:

$$2OCl^- \rightarrow Cl^- + ClO_2 \qquad (11)$$

Direct reaction:

$$Mg + OCl^- + H_2O \rightarrow Mg^{2+} + Cl^- + 2OH^- \qquad (12)$$

Precipitation reactions:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2(s) \qquad (13)$$

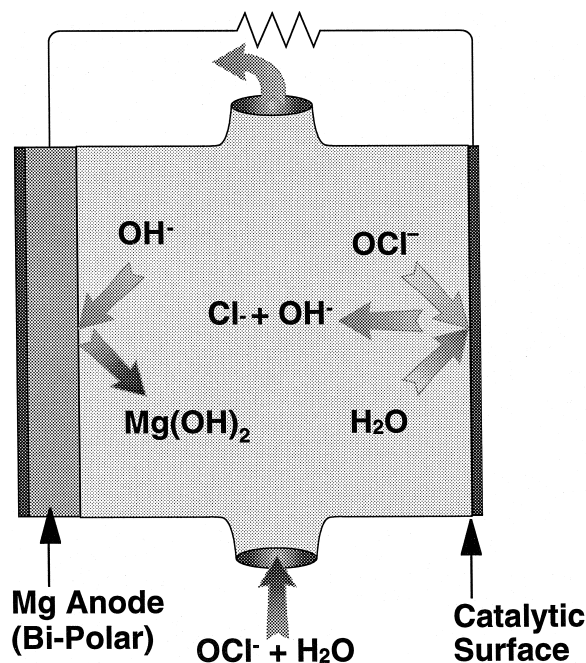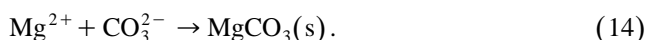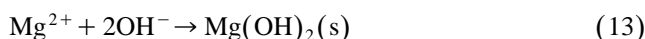$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3(s). \qquad (14)$$
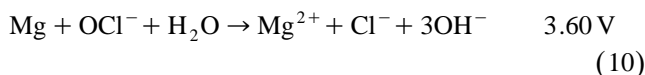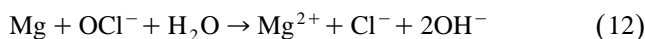
Fig. 1. Schematic diagram of the flowing semi-fuel cell system.

The precipitation reactions are common to both systems and produce solid magnesium hydroxide and magnesium carbonate. The magnesium hydroxide results from the interaction of the magnesium cation with the hydroxyl group produced during the reduction of the catholyte, whereas the magnesium carbonate is a result of the magnesium interacting with the carbonates in seawater.

The electrochemical reduction of the solution phase catholyte (H_2O_2 or NaOCl) occurs on a catalytic surface (Fig. 1) consisting of planar silver, or nickel or carbon catalyzed with palladium and iridium. The presence of the oxidizing agent in solution with the seawater electrolyte provides for an effective electrochemical reduction.

The goals for this project included the evaluation of a magnesium anode with solution phase catholytes, hydrogen peroxide and sodium hypochlorite. The experimental approach was firstly, to determine the corresponding voltages at current densities ranging from 0 to 50 mA cm^{-2} for both systems in a seawater electrolyte both at room temperature and at 50°C, secondly, to ascertain the detrimental effects of the magnesium hydroxide and magnesium carbonate precipitates with time, thirdly, to conduct acid neutralization reactions to combat the precipitation reactions, and lastly, to run continuous tests to determine voltage stability with time.

2. The experiments

Chemicals used included sea salt (ASTM-D 1141-52, Lake Products), sodium hypochlorite (ACS grade, 4–6%, Fisher Scientific), hydrogen peroxide (ACS grade, 33%, Aldrich Chemicals), sulfuric acid (ACS grade, 96%, Aldrich), hydrochloric acid (ACS grade, 36%, Fisher Sci-
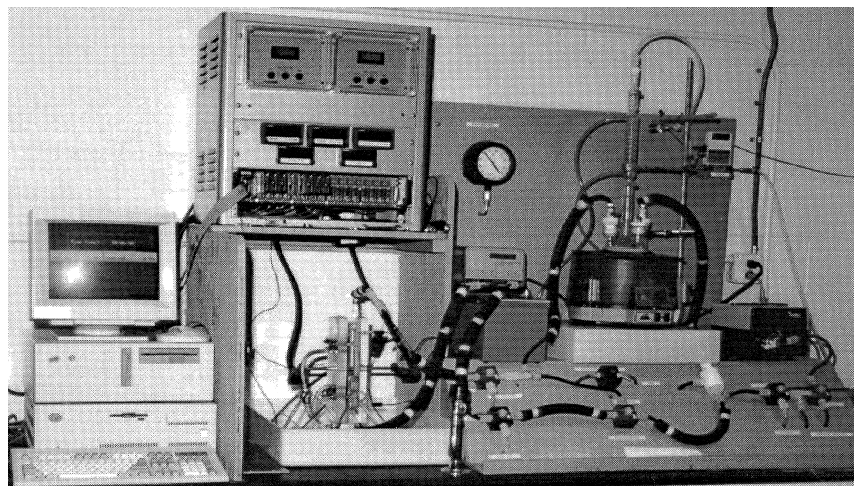
Fig. 2. Photograph of the flowing electrolyte apparatus.

entific), phosphoric acid (ACS grade, 85%, Fisher Scientific) and acetic acid (ACS grade, 100%, Fisher Scientific).

A Model 273A potentiostat/galvanostat (EG & G Princeton Applied Research) was used in a three-electrode configuration for half-cell characterization. The working electrode was the magnesium anode (AZ61). A silver/silver chloride electrode (Ag/AgCl, Fisher Scientific) served as the reference electrode, and the counter electrode was a carbon rod (type L-3089/Grade AGKSP, Bay Carbon).

Full-cell tests were performed in a flowing electrolyte apparatus (Fig. 2). This apparatus consisted of an electrolyte tank (2-litre volume) set into an Electrothermal Unimantle, an Isomatec pump system to pump the electrolyte, a Polystat-Constant Temperature Circulator, a cell holder, a flow loop, a gas monitoring device, a pressure gauge, Omega multimeters, and a data acquisition system. Data were collected using Laboratory Notebook™ and the analysis was performed using Microsoft Excel™.

3. Results

Initial investigations consisted of half-cell polarization profiles to determine the corresponding current density at applied voltages ranging from -1.8 to 0.4 V vs. Ag/AgCl. The size of the working electrode was 0.5 cm^{-2}. Fig. 3 summarizes the results. For the hydrogen peroxide tests, at room temperature (RT) and at 55°C, current densities approaching 200 mA cm^{-2} were observed; whereas current densities of 300 and 500 mA cm^{-2} were observed at room temperature and 55°C, respectively, when sodium hypochlorite tests were performed. At 1.0 V, the current densities for hydrogen peroxide were 20 and 45 mA cm^{-2} at RT and 55°C. For the hypochlorite tests, the current densities were 40 and 85 mA cm^{-2} for RT and 55°C, respectively.

Following these initial evaluations at the half-cell level, full-cell tests utilizing the flowing electrolyte apparatus (Fig. 2) and electrode sizes of 77 cm^{-2} were carried out. Fig. 4 summarizes all the tests carried out at room temperature with a magnesium anode, a silver foil electrocatalyst, a sea-salt electrolyte and a hydrogen peroxide catholyte. The tests were conducted by applying constant currents at densities ranging from 0 to 50 mA cm^{-2}.

The tests conducted with the larger electrodes in the flowing electrolyte apparatus revealed lower current-density ranges. In the seawater only electrolyte, 15 mA cm^{-2} was the highest current density achieved with a corresponding voltage above 1.0 V. Higher current densities were not possible due to magnesium precipitates preventing proper electrolyte flow between electrodes.

Several acids were investigated in an attempt to solubilize the solid precipitates of magnesium hydroxide ($Mg(OH)_2$) and magnesium carbonate ($MgCO_3$) formed in the Mg–H_2O_2 system. The acids tested included sulfuric (H_2SO_4) hydrochloric (HCl), phosphoric (H_3PO_4) and
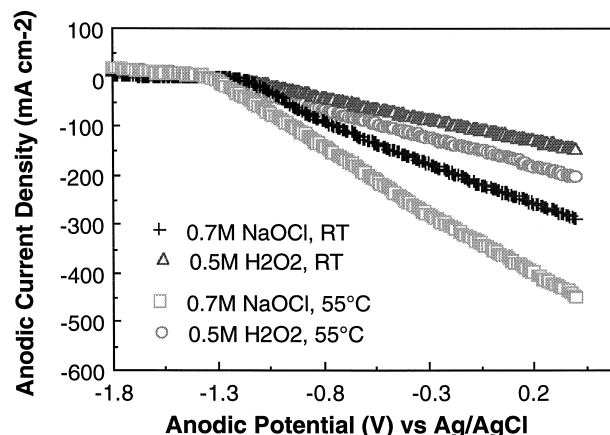

Fig. 3. Polarization profiles for magnesium anodes with hydrogen peroxide or sodium hypochlorites at room temperature and at 55°C.

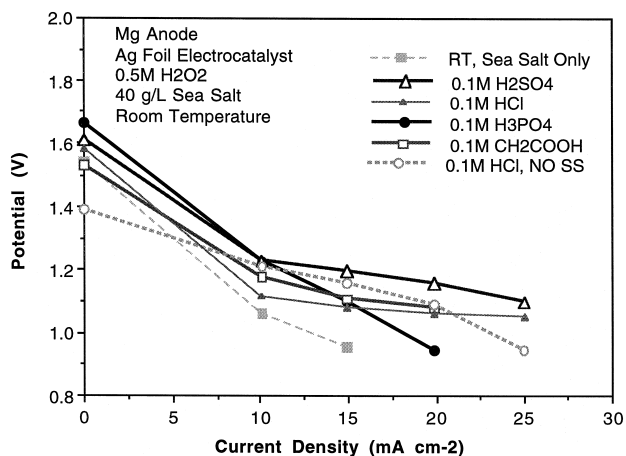Fig. 4. Polarization profiles for magnesium anodes with hydrogen peroxide at room temperature.

Fig. 6. Polarization profiles for magnesium anodes with sodium hypochlorite at room temperature.

acetic (CH_2COOH). All tests were performed with 0.1 M concentration of acid (Fig. 4). The best results were achieved with sulfuric acid. The phosphoric acid tests demonstrated higher open-circuit voltages (OCVs), however, the polarization profiles exhibited increased and undesirable polarizations in the range of 0 to 30 A cm^{-2}.

With sulfuric acid, an initial decline was observed in the polarization profiles, however, the voltage was steady (1.2 V) as the current density ranged from 10 to 30 mA cm^{-2}. All acids, except sulfuric acid, deposited a yellow/grey film on the magnesium surface; this was another advantage observed with the use of sulfuric acid over the other acids tested.

Several tests were also performed using only hydrogen peroxide in distilled water to see if these film effects were due to the components in seawater or the result of the reaction of the acids with the magnesium. The elimination of the seawater did not prevent the formation of the films, therefore the film observed is due to a magnesium acid reaction. Analysis of the films will be carried out using a
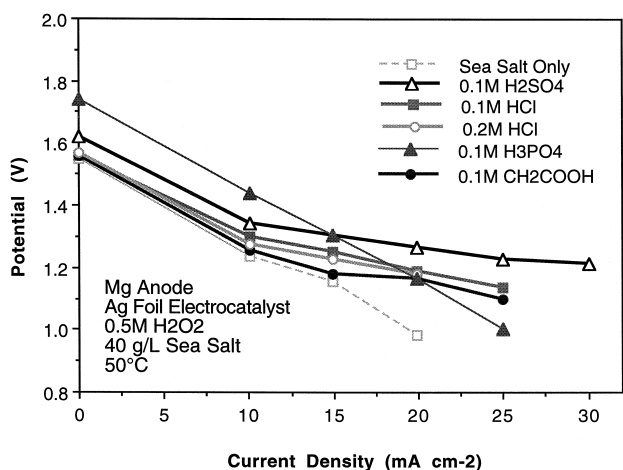
Scanning Electron Microscope with Energy Dispersive Spectroscopy (SEM/EDS) and X-ray Diffraction Spectrometry (XRD). Fig. 5 summarizes the tests repeated at a temperature of 50°C. The trend in results is identical to those observed in Fig. 4.

Magnesium tests with a sodium hypochlorite catholyte were tested next. Fig. 6 illustrates polarization graphs for the magnesium hypochlorite (Mg–OCl$^-$) system (at room temperature) with catalysts of silver foil and nickel foil plated with palladium. Evident from this figure, in comparison to Figs. 4 and 5, is the improvement in voltage at the same current density range (0 to 50 mA cm^{-2}) for hypochlorite over hydrogen peroxide. The voltages observed for the Mg–OCl$^-$ were above 1.2 V for the entire range.

One thing that was noticed during sodium hypochlorite tests with silver foil as the electrocatalyst was a surface reaction of the silver. The silver foil appeared black and discolored—a silver oxide formation is probably the cause. The Mg–OCl$^-$ system when tested did not result in any of

Fig. 5. Polarization profiles for magnesium anodes with hydrogen peroxide at 50°C.
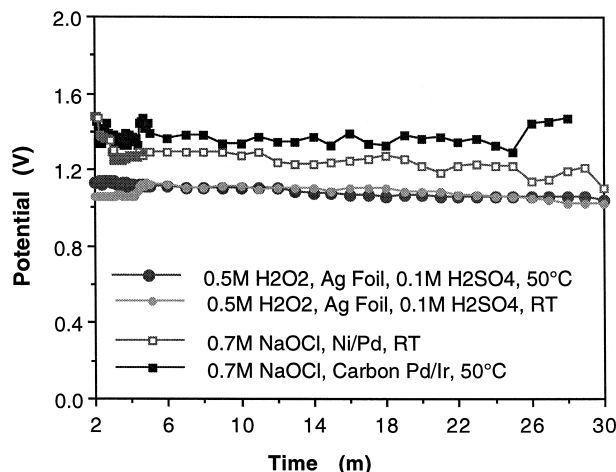

Fig. 7. Variation of potential with time for both hydrogen peroxide and sodium hypochlorite at a constant current density of 25 mA cm^{-2}.

the precipitates observed in the Mg–H_2O_2 system, therefore acid testing was not necessary.

The next set of tests was performed to determine voltage stability with time at an applied constant current density of 25 mA cm^{-2}. Fig. 7 illustrates the voltage profiles for both systems. For the peroxide system, voltages of 1.1 to 1.2 V were observed for run times of up to 60 min. These tests were conducted both at room temperature and at 50°C, with the introduction of sulfuric acid (0.1 M) to the seawater electrolyte in the presence of hydrogen peroxide. The hypochlorite system is also pictured in Fig. 7, the voltages observed being 1.3 to 1.5 V at the temperatures tested.

The electrocatalyst used for the hydrogen peroxide tests was silver foil, however this electrocatalyst was not feasible for the sodium hypochlorite tests. The electrocatalysts used for the Mg–OCl^- testing included both nickel foil and carbon foil catalyzed with palladium and iridium.

4. Summary

A magnesium-solution phase catholyte semi-fuel cell (Mg-SFC) system was investigated as an energetic electrochemical system for low rate, long endurance undersea vehicle applications. This electrochemical system consisted of a magnesium anode and a solution phase catholyte of hydrogen peroxide or hypochlorite, in a seawater electrolyte. The data thus far show extremely encouraging results, however further optimization of both the Mg–H_2O_2 and Mg–OCl^- systems are necessary as well as further characterization of the magnesium electrode surfaces in the different electrolytes.

Acknowledgements

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