The alkaline aluminium/hydrogen peroxide power source in the Hugin II unmanned underwater vehicle

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Abstract

In 1993, The Norwegian Defence Research Establishment (FFI) demonstrated AUV-Demo, an unmanned (untethered) underwater vehicle (UUV), powered by a magnesium/dissolved oxygen seawater battery (SWB). This technology showed that an underwater range of at least 1000 nautical miles at a speed of 4 knots was possible, but also that the maximum hotel load this battery system could support was very limited. Most applications for UUV technology need more power over a shorter period of time. Seabed mapping using a multibeam echo sounder mounted on an UUV was identified as a viable application and the Hugin project was started in 1995 in cooperation with Norwegian industry. For this application, an endurance of 36 h at 4 knots was required. Development of the UUV hull and electronics system resulted in the UUV Hugin I. It carries a Ni/Cd battery of 3 kW h, allowing up to 6 h under-water endurance. In parallel, we developed a battery based on a combination of alkaline Al/air and SWB technology, using a circulating alkaline electrolyte, aluminium anodes and maintaining the oxidant concentration in the electrolyte by continuously adding hydrogen peroxide (HP) to the electrolyte. This concept resulted in a safe battery, working at ambient pressure (balanced) and with sufficient power and energy density to allow the UUV Hugin II to make a number of successive dives, each of up to 36 h duration and with only 1 h deck time between dives for HP refill and electrolyte exchange. After 100 h, an exchange of anodes takes place. The power source consists of a four-cell Al/HP battery, a DC/DC converter delivering 600 W at 30 V, circulation and dosing pumps and a battery control unit. Hugin II is now in routine use by the Norwegian Underwater Intervention AS (NUI) which operates the UUV for high-precision seabed mapping down to a water depth of 600 m. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Aluminium/hydrogen peroxide batteries; Aluminium anodes; Applications/underwater vehicles; Semi-fuel cells

1. Introduction

In 1992/1993, Norwegian Defence Research Establishment (FFI) developed an unmanned underwater vehicle (UUV) powered by a magnesium/dissolved oxygen seawater battery (SWB) [1]. The vehicle was controlled from a surface ship via an acoustic link. The high energy density of the SWB made a large range possible, up to 1200 nautical miles at 4 knots for a 1 ton vehicle. However, because of the low specific power density of the system, power for instrumentation had to be very low.

Looking for applications of this system, we found that near-term potential users of UUVs were not interested in very long range, but required more power for instrumentation (hotel load) than was possible at that time with our SWB technology. Conventional battery technologies gave either low energy (Ni/Cd, lead-acid), or high cost and short cycle-life (zinc/silver oxide).

One interesting application for an UUV was to perform as a platform for a multibeam echo-sounder for the generation of high resolution maps of the seabed. In this application, the UUV cruises below a mother vessel at constant speed and altitude over the seabed with the echo sounder covering a swath of 120°. A typical survey would be a swath width of 170 m at a height of 50 m and a ping rate of 5 Hz. An acoustic positioning system gives the relative position of the UUV to the mother vessel and differential global positioning system (DGPS) gives the absolute position of the mother vessel in global coordinates. Other sensors are used to compensate for orientations and accelerations of the two vessels, making it possible to generate seabed maps with very high accuracy and resolution. The cost of mapping is very dependent on vehicle speed, giving those platforms which do not need to drag a cable through the water a large advantage in deep water.

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In 1995, it was decided to build two UUVs with a depth rating of 600 m for seabed mapping. The first, Hugin I, was equipped with a 3 kWh sealed NiCd battery allowing up to 6 h operation under water. This UUV was used for system development. The second UUV, Hugin II, was equipped with a high energy battery allowing up to 36 h under water. This UUV was delivered to the Norwegian Underwater Intervention AS (NUI) in the summer of 1998 [2] for commercial operation.

Because of extensive experience at FFI with the Al/Air system [3–5], we evaluated the alkaline aluminium/oxygen (gas) system for UUV application. Power and energy densities of this system are high, but the system is complex and the formation of hydrogen from aluminium corrosion in the presence of oxygen must be handled properly. We also found that a system with gas electrodes is most easily handled at constant pressure, thus, it should be contained in a pressure resistant container.

Storage of oxygen in a large vehicle can be made very weight-efficient by using liquid oxygen, but as the vehicle gets smaller, the relative weight and volume of the thermal insulation increase, making compressed gas more favourable. Using state-of-the-art composite containers, approximately 50% of the system weight can be oxygen, as compared to typically 20% with commercial metal gas bottles rated for 300 bar. The density of oxygen at 300 bar is 400 kg m^{-3}. An alternative to the use of compressed gas is to store oxygen as a compound which can be easily decomposed to liberate oxygen. Well-known examples are chlorate candles and hydrogen peroxide (HP). Decomposition of HP liberates 0.471 kg of oxygen per kilogram of pure HP:

$$2H_2O_2 = 2H_2O + O_2. \tag{1}$$

Because concentrated HP is unstable and the reaction (1) is very exothermic, lower HP concentrations are usually used. Commercial HP solutions also contain decomposition inhibitors. In routine use by the industry are 50% and 70% HP, and higher concentrations have been used in torpedoes for many years without accident. An alkaline Al/O$_2$ battery based on HP decomposition for O$_2$ supply was recently published by Alupower [6].

If a battery contains only solid or liquid components, it can work at ambient pressure, making the weight of the battery section independent of the design pressure. This modus is used with many battery chemistries and is called pressure-compensated or pressure- balanced operation. The advantage of balanced operation is that the weight of the pressure hull increases with design depth and as the vehicles mass in water should be equal to its displacement (neutral buoyancy), the ability to bring weight (batteries and instruments) inside the pressure hull decreases with design depth. By placing the battery outside the pressure hull, only the weight of the battery in water must be compensated. To use this concept with the alkaline aluminium system requires the oxygen or HP to be dissolved in the electrolyte. One advantage of HP over oxygen gas in ambient pressure batteries and fuel cells is that HP can be stored in a plastic bag at ambient pressure and added to the electrolyte by a simple metering pump. In contrast, oxygen from gas bottles must be delivered against a pressure which increases with depth and with decreasing oxygen pressure in the tank. For a deep dive, such as to 3000 m, the water pressure is 300 bar and the amount of energy required to take the oxygen out of the gas bottle is quite significant.

2. Cell chemistry

The overall cell reaction in the alkaline Al/HP cell is:

$$2Al + 3H_2O_2 + 2OH^- = 2Al(OH)_4^-. \tag{2}$$
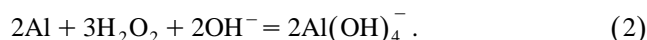
Whether HP is reduced directly at the cathode according to:

$$3H_2O_2 + 6e^- = 6OH^-, \tag{3}$$

or is decomposed at the cathode surface or in the electrolyte according to:

$$3H_2O_2 = 3/2O_2 + 3H_2O, \tag{4a}$$

followed by reduction of oxygen:

$$3/2O_2 + 3H_2O + 6e^- = 6OH^-, \tag{4b}$$

does not affect the overall cell reaction.

We observed that the direct corrosion reaction of HP with Al according to Eq. (2) is rapid and that the rate increases rapidly with the concentration of HP in the electrolyte. It also increases with the surface area of the anode and with the velocity of the electrolyte over the anode surface. Because of the large negative enthalpy of this reaction, heating of the electrolyte takes place. This will also be the case for the direct reaction of aluminium with oxygen dissolved in the electrolyte:

$$2Al + 3/2O_2 + 2OH^- = 2Al(OH)_4^-. \tag{5}$$
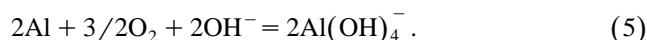
Together, the loss of aluminium through the direct reaction with oxidant according to reactions (2) and (5), plus loss of aluminium through reaction with water:

$$2Al + 3H_2O + 2OH^- = 2Al(OH)_4^- + 3H_2, \tag{6}$$
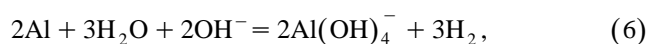
and loss of oxygen gas to the surroundings have a large impact on the practical performance of the alkaline Al/HP system. In absence of losses, the production of one Faraday consumes 9 g Al, 17 g of 50% H$_2$O$_2$ and 62 g 7 M KOH. This corresponds to 305 A h kg^{-1} of reactants.

3. Principles of battery design

Descriptions of Al/HP batteries, wherein HP is added to the electrolyte, have been published by Zaromb [7] and
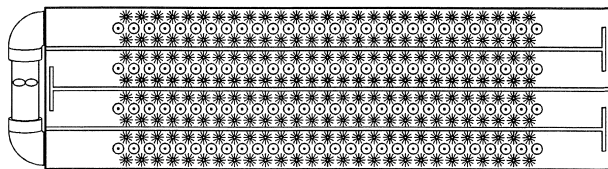
Fig. 1. Top view of the four-cell Al/HP battery. * = Bottle-brush cathodes; O = magnesium anodes. The circulation pump is to the left.

others. Generally, they can be divided in two groups, ones with a common electrolyte and others with HP addition to the catholyte and a semi-permeable membrane separating the anolyte and the catholyte. The advantage of the separate electrolytes is that a high HP concentration in the catholyte can be used without having high losses caused by the direct reaction between aluminium and HP, according to reaction (2). The disadvantage is, of course, a more complicated battery. An elegant cell design, using separate catholyte and anolyte, was recently published by Marsh et al. [8]. This cell is fed from the back with HP and uses the porous cathode as separator, allowing very high current densities with only a low concentration of HP in the electrolyte.

3.1. Dimensioning the UUV battery

Considering the simple construction of a battery using a common circulating electrolyte and assuming that we would be able to get sufficient performance even with a very low concentration of HP or oxygen in the electrolyte, we decided to use the common circulating electrolyte concept and add HP directly to the electrolyte.

For this particular application, we needed 600 W at a voltage level of 30. Rapid recharge (in less than 30 min) was important. Exchange of electrolyte and refill of HP can be done very rapidly, whereas exchange of anodes is

more laborious, taking typically 2 h. Thus, we decided on an anode capacity sufficient for three dives or 100 h of discharge and an amount of electrolyte and HP sufficient for 36 h. A typical operation would be two dives of up to 36 h, each followed only with liquid refuelling, followed by an exchange of anodes and refilling of electrolyte and HP after the third dive. The battery was to operate at ambient pressure. Because of the relaxed safety regulations associated with the use of 50% vs. 70% HP, 50% was selected, in spite of the better performance obtainable with 70%. However, the battery can at any time use 70% HP.

In the AUV Demo [1], we used a large single cell battery with a DC/DC converter. With the Al/HP battery, we also wanted to use a DC/DC converter to increase and stabilise the output voltage, but decided to use serially connected cells to decrease the battery current and to reduce the weight and cost of the conductors and the DC/DC converter. From considerations of leakage current (which increases rapidly with cell number) and the other design parameters, the number of serially connected cells was set to four.

In AUV Demo, we used bottle brush cathodes [9] and cylindrical Mg anodes and the number of anodes and cathodes were approximately equal. The oxygen concentration in seawater was approximately 0.3 mM and the conductivity 30 mS. By changing from seawater to 7 M KOH, the electrolyte conductivity increased by an order of magnitude and through addition of HP, the concentration of the oxidant could be varied at will. However, we wanted to run the cell with as low an oxidant (HP and O_2) concentration in the electrolyte as possible in order to decrease the losses by reactions (2) and (5). Because of this, the cells were made with one row of anodes and two rows of cathodes to maximise the ratio between cathode and anode area. Fig. 1 shows the battery.
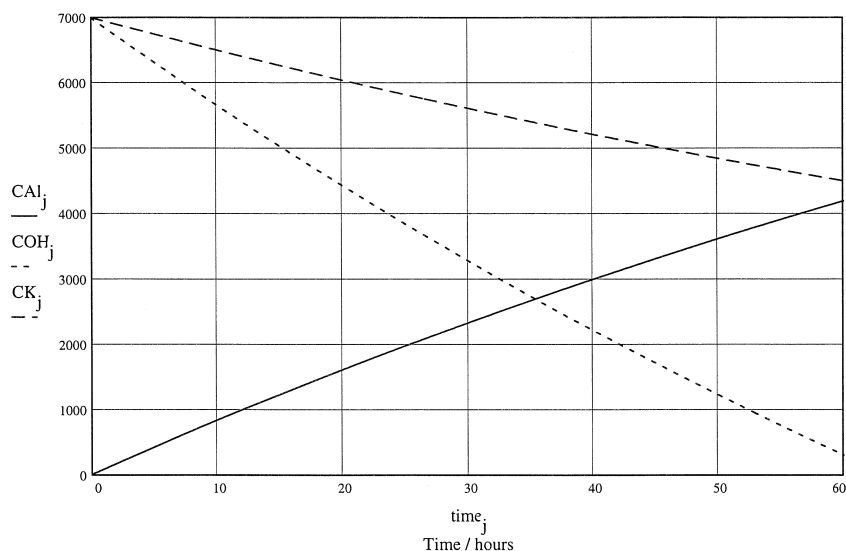

Fig. 2. Simulation of the variation of the concentration (in mol m^{-3}) of OH$^-$, K$^+$ and Al(OH)$_4^-$ vs. time (in hours) at a constant current load.

In addition to the battery case, the system consists of two plastic bags for 50% HP, one on each side of the battery. The battery also contains a compressible electrolyte reservoir, a one-way electrolyte discharge system, an axial pump for electrolyte circulation and a metering peristaltic pump for HP addition. As HP is added to the electrolyte, an increase in volume takes place. This opens up two different configurations: constant mass and constant volume. In both cases, the buoyancy of the battery will vary with time, thus, an active buoyancy system is mandatory. Constant mass gives a slightly higher energy density, but a more complicated gas separation system. Thus, we decided for constant volume. In this case, a one-way valve to the ocean relieves both excess gas and electrolyte. Fig. 2 shows calculated concentrations of OH^-, K^+ and $Al(OH)_4^-$ vs. time in a cell with constant volume. The data are based on an excess of 25% for HP and a Faradaic efficiency of 0.8 for Al (including HP, O_2 and H_2O corrosion). Cell volume is 25.5 l and the discharge current is 141 A.

It is seen from Fig. 2 that with time, the concentration of $Al(OH)_4^-$ increases and the concentration of OH^- falls. In real experiments, however, this decrease in OH^- stops when aluminium hydroxide precipitates:

$$Al(OH)_4^- = Al(OH)_3 + OH^-. \tag{7}$$
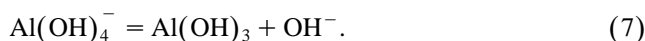
In our system, precipitation does not take place until after approximately 40 to 50 h of discharge. In our experience, precipitation should be avoided in order to ensure easy pumping of the electrolyte and to keep the cathodes clean. We have observed that to be on the safe side, the discharge should end before the hydroxyl concentration falls below that of the aluminate, At this aluminate concentration, the solution is highly supersaturated with respect to reaction (7) and the used electrolyte should not be left in the battery. Precipitation is followed by an immediate increase in electrolyte conductivity, leading to a small increase in cell voltage. In an emergency and given sufficient HP and aluminium, discharge may continue, but a decreasing cell voltage caused by a partial clogging of the carbon fibres will be observed. The need to work with a clear electrolyte is the main factor determining the energy density of this system.

3.2. Gas separation system

Gas handling is very important. Part of the HP in the electrolyte decomposes according to reaction (1). As the solubility of oxygen in the electrolyte is very low, small oxygen bubbles form and rise to the surface. As the UUV dives, the bubbles compress and the volume of electrolyte decreases. Through the use of a compliant rubber membrane, this volume decrease is accommodated without generating a negative pressure difference over the battery. This effect is most important close to the surface where the relative change of gas volume with depth is largest. As the

UUV goes deeper, the solubility of oxygen increases and oxygen will be consumed by the cathode reaction. This effectively reduces oxygen loss through reaction (1).

For hydrogen, however, no consuming reactions exist and as soon as the electrolyte is saturated, bubbles form and must be discharged via the gas separation system. On ascent, the pressure decreases and a significant volume of gas forms which must be handled by the gas separation system.

3.3. Thermal control

Thermal control of the battery is also essential. The over-voltages of both the anode and the cathode reactions are high. In addition, the aluminium corrosion according to reactions (2), (5) and (6) may generate large amounts of heat. An increase in temperature decreases the anode po-
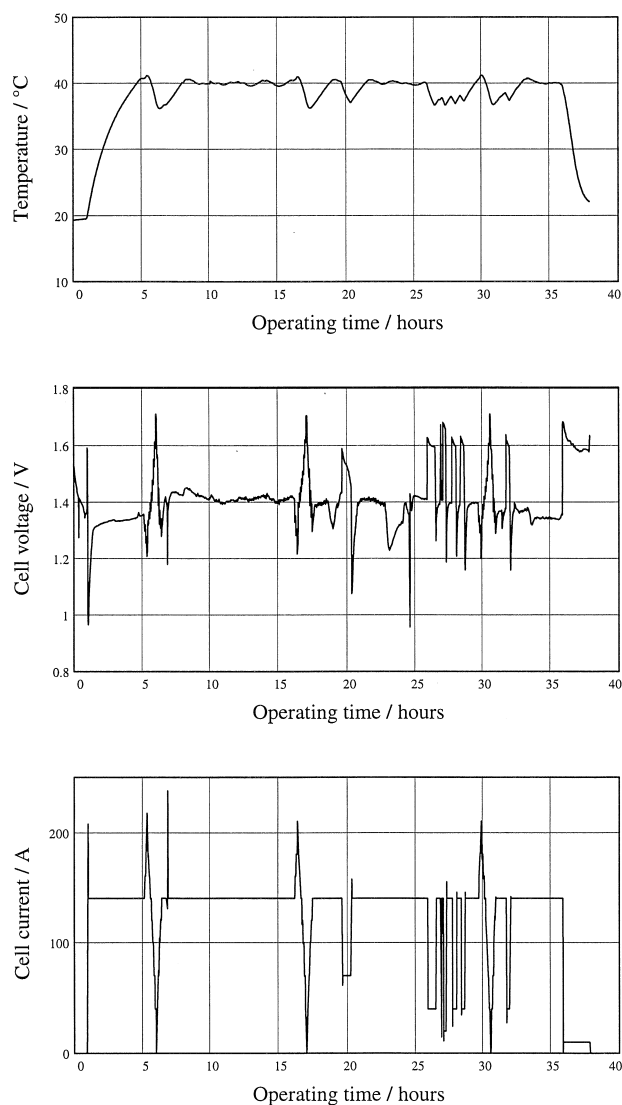

Fig. 3. Discharge of a single cell. Upper curve: electrolyte temperature, centre: cell voltage, lower curve: cell current.

tential and increases the electrolyte conductivity. Both factors increase the cell voltage. On the other hand, corrosion causing hydrogen evolution increases very rapidly with temperature. Also, decomposition of HP and corrosion via reaction (2) increases with increasing temperature. These factors make 30 to 40°C an optimum temperature for this system. Heat production as a function of load and HP excess was calculated from a thermal model based on tabulated thermodynamic values for the chemical reactions of interest. Results from these calculations were used to evaluate different methods of electrolyte cooling. Given the low temperature of Norwegian seawater, thermal control was based on passive heat flow through the battery case. This mode was verified with a complete battery case built with electrolyte flow and electric heaters and tested when immersed in water.

Due to the large heat capacity of the battery and the reduced power demand (the propulsion motor is not in use), the UUV can still be operated on board the mother ship for several hours before deployment of the UUV must take place. During this period, however, cooling of the DC/DC converter container by flushing with water may be necessary.

4. Battery development

The cathodes were of the carbon fibre, bottle brush-type with nickel cores. Brush diameter was 30 mm. Evaluation of the cathode catalyst was done in a 10-cathode, four-anode, flow cell. The height of the electrodes was 100 mm. The electrolyte was 2.5 litres of 7 M KOH circulating at
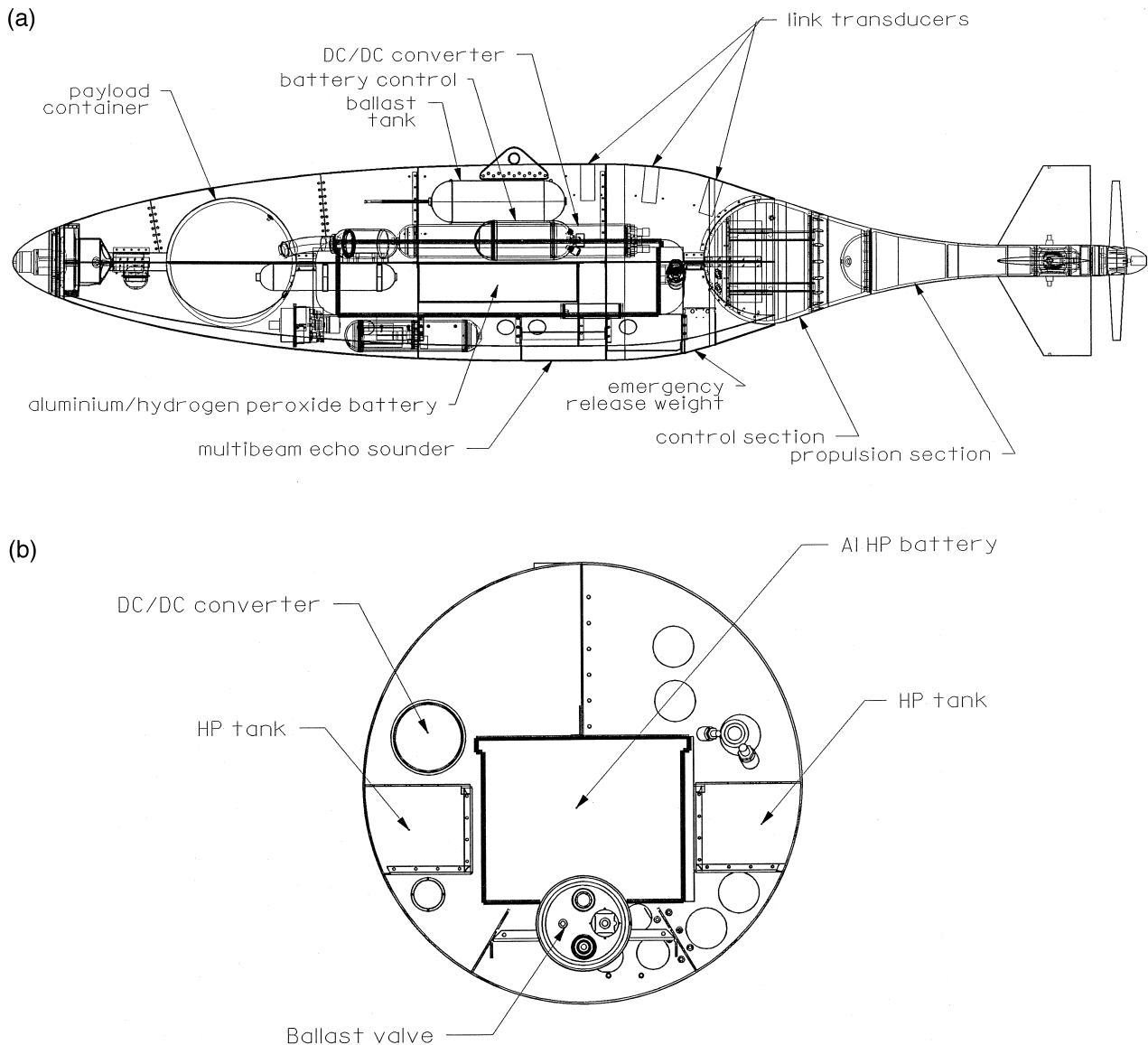

Fig. 4. The Hugin II UUV. (a) Side view. (b) Cross-section.

15 1/min. The anodes were connected together, but each cathode in the cell was discharged separately at 1.00 A and its cell voltage and the anode potential vs. a saturated calomel reference electrode (Radiometer K401) were logged with a Hydra (Fluke) 2620A. In order to prevent degradation of the reference electrode, it was situated in a Luggin capillary filled with 3% KCl and 3% agar. The concentration of HP in the electrolyte was determined by titration with 0.002 M $KMnO_4$ solution after acidification with 5 M H_2SO_4.

Full-scale single cells were tested at variable pressures in a high-pressure tank down to a depth of 100 m (1.1 MPa). In these experiments, hydrogen evolution was continuously measured using a Rexnord model 500 combustible gas detector. Full-scale batteries were discharged both in a cooled-water tank with forced circulation at atmospheric pressure, and in the Hugin II UUV in the ocean.

5. Results

Fig. 3 shows a typical discharge of a full-scale single cell. This was the third discharge with the same set of anodes, thus, the ohmic losses in the electrolyte (IR) were at their highest. Initially, the cell temperature is low, but stabilises at 40°C after 4 h of discharge. During most of the time, the cell voltage varies between 1.2 V at 220 A to 1.7 V on open-circuit. Current/voltage curves were recorded at approximately 6, 17 and 31 h. During the discharge, we also varied some of the other factors determining cell voltage and anode corrosion rate such as pressure, rate of circulation and HP excess factor. As an example, at 23 h, the pressure was reduced from 1.1 MPa to 0.1 MPa (surface pressure). The reduced cell voltage is caused by reduced oxygen solubility. By increasing the HP excess factor, normal cell voltage is restored. An increase in pressure to 1.1 MPa was done at 25 h and reduced to normal at 33.5 h.

Fig. 4 shows the Hugin II UUV. The vehicle has a volume of 1.2 m^3. Propulsion is by a slowly rotating propeller and roughly 300 W is used for propulsion at a speed of 4 knots. Total load on the power source is 520 W. The load on the Al/HP battery is approximately 800 W corresponding to a DC/DC converter efficiency of 65%.

The UUV is operated from a 40 ft container which, in addition to the launch and retrieval systems for the UUV, also contains a water purification system and tanks for pure water, HP, KOH and waste. The liquids are handled using low-pressure pumps, flexible tubing and 'no-drip' connectors which only mate with the right connector. This allows for safe operation even in rough weather. During launch and retrieval, a special system stops excess electrolyte from being released by the UUV, but during the mission, electrolyte is continuously released from it. This electrolyte is classified as 'environmentally harmless'. Af-
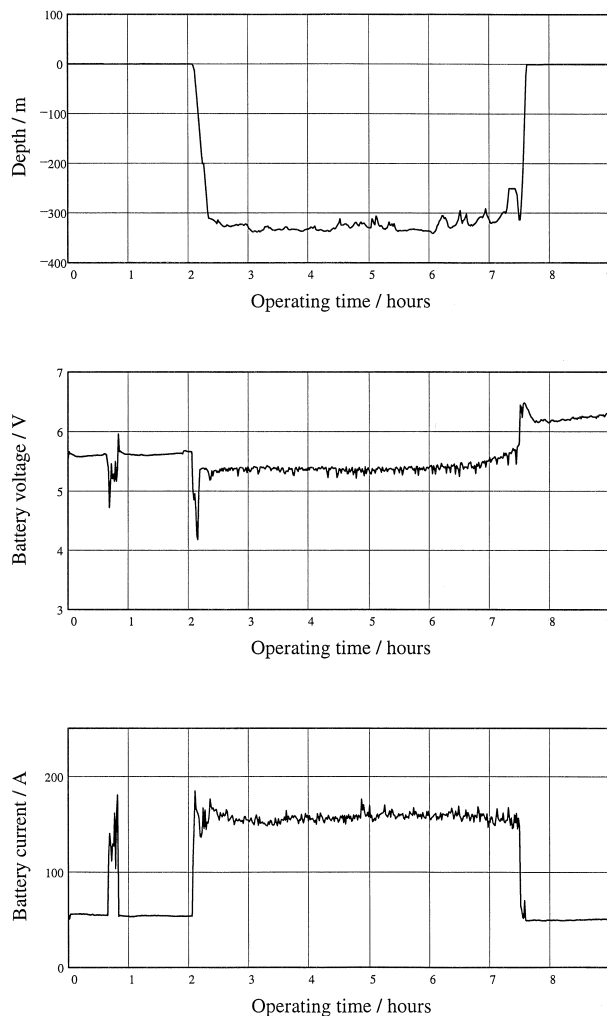

Fig. 5. Operation of an Al/HP battery in Hugin II. Upper curve: depth, centre: battery voltage, lower curve: battery current.

ter the mission, excess electrolyte is dumped to the waste tank. In the open ocean, spent electrolyte can also be discharged overboard after dilution with seawater. In addition to the precautions mentioned above, all personnel involved use protective clothing and eye protection.

Fig. 5 shows the battery performance during a dive performed by NUI on 26 June 1998, outside Bergen. After 2 h on deck, all subsystems in the UUV were found OK and the UUV deployed. It then dived to 320 m and cruised for 5 1/2 h before recovery. Nine hours after activation, the electrolyte was emptied and the battery flushed with pure water. Because of the short duration of this dive, the electrolyte was stored and reused later.

6. Discussion

Compared to other low-rate batteries with a common circulating electrolyte (Al/HP batteries such as the bipolar battery currently under development by NUWC Newport

[9,10]), our battery has the advantage of being mechanically rechargeable. It operates at an HP concentration of 3 to 5 mM, compared to 250 mM in the bipolar battery. The Faradaic efficiency of our battery with respect to aluminium is between 80 and 90% compared to 60 to 75% for the bipolar battery. However, a fair comparison of the two batteries is not possible until an operational system, that is neutrally buoyant and seaworthy, is presented.

Through the operation of the Hugin II UUV, it has been demonstrated that this alkaline Al/HP battery system is well-suited for deep sea applications. However, there is still room for improvement of the UUV-system, partly in terms of increased specific energy of the power source and partly through more efficient use of the available power. The greatest losses are caused by the DC/DC-converter. The efficiency of the present unit is much lower than expected, and a redesign is under way. (With AUV-Demo, we reached 80% converter efficiency; with Hugin II, the efficiency is only 65%.) A reduction in the use of auxiliary power for the battery (electrolyte circulation pump, HP dosing pump and battery control) is also possible. An increase in the life of the cathode catalyst from the present level of 600 h before reapplication of new catalyst would be of interest for some applications. An increase in the cathode potential would also be beneficial.

However, even at the present level, this alkaline Al/HP power source is unique both in terms of energy density for a neutrally buoyant system and in terms of rate of recharge. With the present amount of aluminium in the battery, the energy content of the UUV can be increased simply by increasing the amount of electrolyte and HP for a mission. Alternatively, by reducing the amount of aluminium to the requirement of only one mission, and compensating the reduced aluminium weight with an increase in the amount of HP and electrolyte, an increase in the energy available for the mission can be made.

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