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Design of a dome-shaped aluminium water battery

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Aluminium/water batteries using hydrogen evolving cathodes are one of the candidate batteries for sub-sea application. However, it is impractical to use parallel plate construction because the significant increase in the anode-cathode gap during long term anodic discharge leads to unacceptable iR losses. A conceptual design, using a dome-shaped configuration, is presented and preliminary tests on a prototype show that such a battery can ensure constant anode–cathode gap and uniform anode dissolution. The energy density of such a battery for a two year period is estimated to be 855 Wh kg^{-1}.

1. Introduction

There is a need to develop cableless systems for sub-sea operations. The presently available power sources are not capable of satisfying the long term requirements for sub-sea operation. Metal/water batteries either using hydrogen evolving [1] or oxygen reducing [2] cathodes are one of the most promising candidates. Such batteries give a very high theoretical energy density since only the anode is consumed. An essential feature of this system is that the design of the battery must have stable discharge characteristics. Such batteries ideally should have: (i) invariable anode surface area during discharge; (ii) invariable anode-cathode gap all the time; (iii) minimum anode surface area/volume ratio to minimise the self discharge; and (iv) the products of reaction should be able to discharge into the sea readily and not clog the cell.

Conventional metal/water batteries use flat anode and cathode plates. The anodic surface area remains constant under uniform dissolution. However, even at moderate current density of 10 mA cm^{-2} (for batteries using hydrogen cathode), the depth of dissolution of an aluminium anode over one year will be 10.9 cm. This will result in unacceptable iR loss of 2.73 V since the resistivity of sea water is typically 25 Ω cm [3]. This means that the battery would not be able to produce any power. Therefore, there is a need to consider alternative battery designs which can maintain the anode–cathode gap at a constant value. One approach is to use the wedge-shaped anode structure [4]. The anode is lowered by gravity to maintain the distance between anode and cathode. The disadvantage is that the distribution of current on a wedge-shaped surface is not uniform. The edge effect results in high local current densities which can damage the cathode [5] and this will also change the wedge shape due to nonuniform discharge.

The design of a dome-shaped battery structure and a preliminary evaluation of a prototype is presented in this paper.

2. Some basic theoretical and practical considerations

In undertaking any conceptual design of battery systems, it is necessary to fix some performance parameters. In the case of an aluminum/sea water battery used in sea water environments, the following parameters were chosen for the initial conceptual design: an output voltage of 12 V; a power output of 25 W; a total current output from each battery of 25 W/12 V = 2.08 A; and an operating life of two years.

Results to date have indicated that a single Al/H_2O battery gave 0.5 V at 10 mA cm^{-2} even at 5° C [6]. Since there are unavoidable losses due to shunt current when the batteries are connected in series, a 20% voltage loss is assumed. In other words, the available voltage from each cell is assumed to be 0.4 V. Therefore, the total number of cells required is 12/0.4, i.e. 30.

The volume of aluminium in each cell is calculated as follows:

$$V = \frac{itN}{Fd} \tag{1}$$

where: I, the current, is 2.08 A; t the time is $3600 \times 24 \times 365 \times 2 = 63\,072\,000$ s; N, the electrochemical equivalent of Al, is 9 g mol^{-1}; d, the density of Al, is 2.698 g cm^{-3}; and F, the Faraday constant, is 96 500 C mol^{-1}. Therefore, the total volume of aluminium per cell is 4534 cm^3.

For long term operation, the ratio of surface area to volume for a consumable anode should be taken into account since the anode is subject to self-discharge. The percentage of self-discharge relative to the discharge current is very high under low operating

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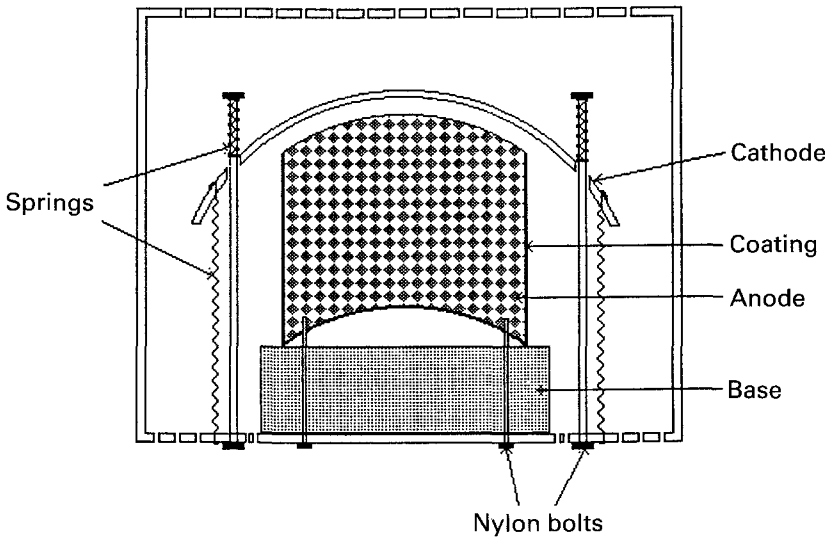

Fig. 1. Conceptual design of an aluminium/water battery.

current densities. At $10\,\mathrm{mA\,cm^{-2}}$, the minimum surface area of each anode should be $2.08 \times 1000/10$, i.e. $208\,\mathrm{cm}^2$, in order to ensure an output of 2.08 A from each cell. Therefore, the ideal aluminium anode should have a surface/volume ratio of 208/4534, i.e. 0.0459, to minimize the needless exposure of the aluminium anode surface to sea water, since the greater the exposure area, the higher the amount of parasitic reaction due to self discharge. For various normal geometries, none of the shapes can approach the ideal value of 0.0459, although the spherical and semispherical shapes ($S/V = 0.349$) are significantly better than other shapes. Since the current distribution on a spherical surface is very uniform, a more acceptable design may, therefore, be as follows: a long cylindrical rod with a hemispherical dome, whose surface area equals the operating area, $208\,\mathrm{cm}^2$. The rest of the cylinder will be coated with protective paint which falls off as the hemispherical top is gradually corroded away. Moreover, change of surface area can be avoided when a spherical geometry anode is used. If the cathode is configured into a hemisphere dome and separated from the anode by means of widely spaced insulating polymer strips, the anode–cathode gap will also be invariant, provided the aluminum anode undergoes uniform dissolution. The anode should retain its hemispherical shape with time. Fig. 1 shows a schematic diagram of such a design. Springs are provided to ensure that the anode–cathode gap is kept constant.

Figure 2 shows the schematic diagram used in the detailed calculations for various designs. The operating area of the anode should be equal to the crown area of the sphere, A:

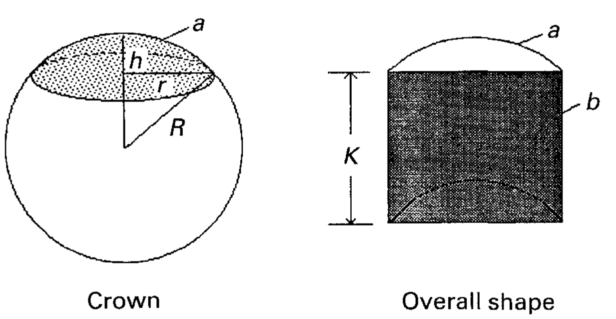

Fig. 2. Schematic representation of an aluminium anode structure: (a) operating surface and (b) protective coating.

$$A = 2\pi Rh \tag{2}$$

and the volume of each battery is

$$\begin{aligned} V &= \pi h^2(R - h/3) + \pi r^2 K - \pi h^2(R - h/3) \\ &= \pi r^2 K \end{aligned} \tag{3}$$

such that

$$r = SQR[R^2 - (R - h)^2] \tag{4}$$

Substituting Equations 2 and 4 into Equation 3, and rearranging, gives

$$\pi h^2 K - AK + V = 0 \tag{5}$$

Equation 5 is a polynomial equation and the solution was calculated by using a simple computer program written in GWBASIC. The results for the dimensions of aluminium anodes of various shapes for an Al/H_2O battery operated for two years are reproduced in Fig. 3 and Table 1.

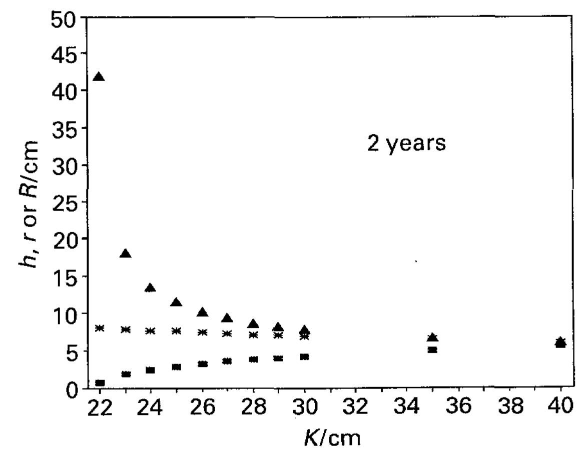

Fig. 3. Relationship between K and h (■) or r (∗) or R (▲) for a two-year battery.

Table 1. The structural factors of the aluminium anode (two years)

K/cm	h/cm	r/cm	R/cm
22	0.79	8.11	41.91
23	1.83	7.93	18.08
24	2.44	7.76	13.55
25	2.90	7.61	11.44
26	3.26	7.46	10.17
27	3.56	7.32	9.34
28	3.82	7.19	8.67
29	4.05	7.06	8.19
30	4.25	6.94	7.80
35	4.99	6.43	6.64
40	5.48	6.01	6.04

3. Construction and performance of a prototype dome-shaped aluminium/water battery

A prototype dome-shaped battery was assembled with an AlSnMgGa alloy (containing 0.14% Sn, 0.63% Mg, 0.04% Ga and 0.0018% Fe) anode and a hydrogen cathode. The alloy anode was fixed on a base and the exposed surface area was $5\,cm^2$. The base had three nylon threads for locating the cell in place. The cathode was a dome-shaped 60 nickel mesh, coated with Pt/WO_3 hydrogen evolution catalysts (catalyst loading $\sim 2\,mg\,cm^{-2}$, Pt $\sim 0.2\,mg\,cm^{-2}$) [7]. The nickel screen was spot welded onto a stainless steel cathode holder, which had three equally spaced holes for locating the cathode assembly in a vertical position. In addition, there were three stainless steel springs, to keep the anode–cathode gap constant. A polyethylene mesh was used as separator.

The basic electrochemical reactions are as follows:

$$2Al + 6OH^- \rightarrow 2Al(OH)_3 + 6e^- \quad \text{(anodic)} \quad (6)$$

$$2H_2O + 2e^{-1} \rightarrow H_2 + 2OH^- \quad \text{(cathodic)} \quad (7)$$

Figure 4 shows the performance of a dome-shaped battery operating at $10\,mA\,cm^{-2}$ after a test period of 5 h. The surface area of the anode was $5\,cm^2$. The battery was tested at room temperature with 3% NaCl solution. The performance was almost the same as that for flat plate batteries, confirming that the basic design is sound, though longer term tests have to be done.

One of the advantages of such a battery is the high energy density. For a 25 W battery, an operating current density of $10\,mA\,cm^{-2}$ is assumed and two cells are connected in series to obtain an output voltage of 0.8 V (20% of voltage loss due to shunt current is taken into account for each cell). Therefore, the total area of anode or cathode is $0.625\,m^2$. The amount of aluminium alloy in two years, including 20% self discharge, is 442 kg. By assuming 20 kg for the weight of cathode and 50 kg for the weight of current collectors, reinforcing structures, etc., the total dry weight of the battery is 512 kg. This results in an energy density of $855\,Wh\,kg^{-1}$. It is important to note that the energy density of the best primary lithium battery is $500\,Wh\,kg^{-1}$ [8]. For sub sea applications, the normal operating voltage of the power source is 12–15 V. The reason for connecting two batteries in series in this design is that the voltage can be readily increased to 15 V by the use of a recently invented d.c. to d.c. converter [9]. This converter can convert a 0.7 V power source to a 15 V power source at an efficiency of $\sim$ 80%. Therefore, the energy density of an aluminium/water battery/d.c. converter system is $\sim 684\,Wh\,kg^{-1}$.

3. Discussion

The shape of the crown is dependent on the parameters *K*, *h*, *R* and *r* for a given surface area. *R* is inversely proportional to *K*, and the crown tends to a plane at the lowest *K* value. In this case, the surface area of the cylinder, which needs to be protected, is also the lowest. On the other hand, the crown tends to a standard hemisphere when *K* increases infinitely, resulting in a maximum surface area for the cylinder. Figure 5 shows the surface area of the cylinder at different *K* values for a two-year battery. In principle, the probability of mechanical damage to the surface of the cylinder is higher when the surface area of the cylinder is high and vice versa. It is known that the distribution of current on a spherical surface is far

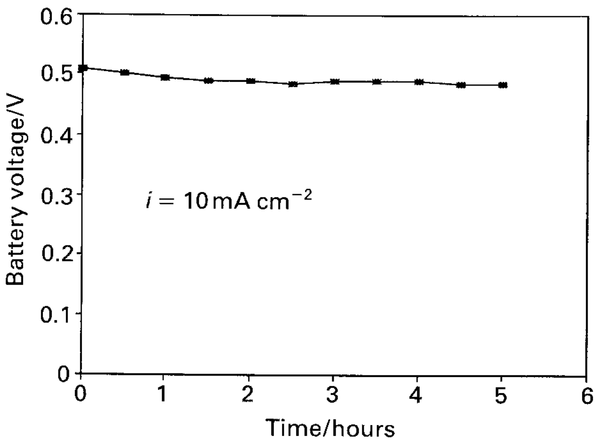

Fig. 4. The performance of a dome-shaped aluminium/water battery in 3% NaCl solution at room temperature.

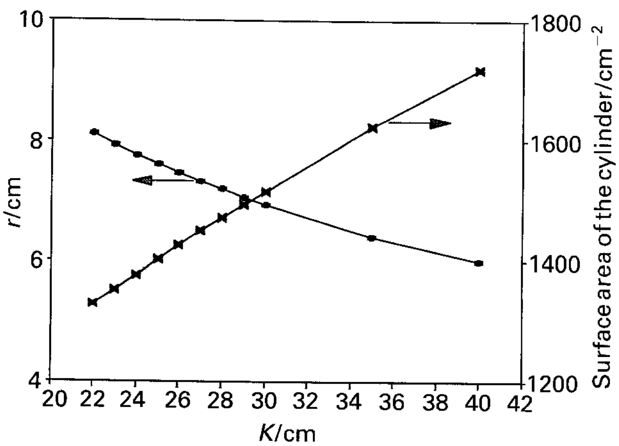

Fig. 5. The surface area of the cylinder at different *K* values for a two-year battery.

more uniform than on a wedge-shaped surface, because the current density on the apex is much larger than on the planes which give rise to the so-called edge effect. Therefore, the optimal electrode geometry is a dome-shaped cylinder.

It should be noted that the amount of anode material consumed during operation is higher than that calculated, because of self discharge. Therefore, Equation 1 should be modified by introducing a coefficient, which is dependent on the self discharge rate of the anode material used.

The basic advantages of a dome-shaped full battery over the conventional plate battery are that the exposed aluminium anode surface is limited to the operating anode surface, hence self-discharge is reduced to a minimum and the cathode–anode gap remains constant. Moreover, the reaction products are more readily washed away on a dome-shaped surface.

Further work is in progress on sea trials. Apart from unavoidable testing in the laboratory for quality control purposes, all subsequent tests will be done in offshore environments.

Acknowledgement

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