

Development of an aluminium/sea water battery for sub-sea applications

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Abstract

There are two modes of operation for an aluminium/water battery: use of hydrogen-evolving or oxygen-reduction cathodes. In the first case, the current density is $\sim 10 \text{ mA cm}^{-2}$ at 0.5 V. This leads to significant increase of pH and deposition of Ca/Mg(OH)_2 at the cathode, leading to sharp decrease in battery performance. On the other hand, in the oxygen-reduction mode, the current density is $\sim 0.1 \text{ mA cm}^{-2}$ at 1.4 V, because of the low concentration of O_2 in sea-water. Long-term tests of an Al/water battery using Teflon-bonded $\text{Co}_3\text{O}_4/\text{C}$ oxygen reduction cathodes in Brightlingsea Harbour, Essex, over a test period of 70 days have shown that the performance of this battery is stable and that it is possible to increase its performance by means of multi-cathodes on either side of the anode. A conceptual design shows that such a battery has an energy density of 1008 Wh kg^{-1} over an operating period of one year, significantly higher than all the conventional primary batteries considered for use in sub-sea environments.

Introduction

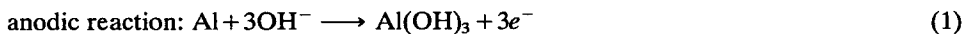
The growing interest in sub-sea production and exploration of oil and gas wells has created the need to develop long-life and high energy density batteries. Primary lithium batteries have the highest energy density (up to 500 Wh kg^{-1}) [1], but if these batteries are used for sub-sea applications, there is a need to put them inside pressure vessels, reducing their energy density and increasing the operating cost. On the other hand, primary batteries based on the use of metal alloy anodes and oxygen-reduction or hydrogen-evolution cathode should be able to satisfy the above requirements [2–5]. Sea-water is used as the electrolyte and dissolved oxygen or water is used as the oxidant. Therefore, the only consumable item is the metal anode since dissolved oxygen and water are supplied by sea-water. Moreover, since sea-water is used as the electrolyte, the battery does not require vessel containment.

Some theoretical and practical considerations

Electrode reaction processes

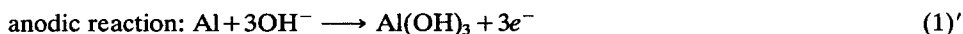
Metal/water batteries can be operated under two modes:

- (i) Mode 1 (using a hydrogen-evolving cathode)



The operating voltage of such batteries is about 0.5 V at a current density of $\sim 5 \text{ mA cm}^{-2}$.

(ii) Mode 2 (using an oxygen-reduction cathode)



The operating voltage of such batteries is about 1.4 V at a current density of $\sim 0.1 \text{ mA cm}^{-2}$. The low current from such batteries is due to the limited solubility of oxygen in sea-water.

Natural sea-water contains dissolved salts, dissolved gases, organic substances, colloidal matter, and particulates, both living and detrital. Most of the compounds of sea-water are unreactive electrochemically [6]. Easily reducible species at the cathode are dissolved oxygen, water and hydrogen carbonate. The formation or precipitation of insoluble salts of calcium and magnesium through alkalisiation of the cathode surface by reactions (2) or (3) is detrimental, which will greatly reduce the output voltage of the battery.

Oxygen is an extremely electroactive constituent of sea-water. The theoretical half-cell potential for the reduction of oxygen in pH 8.2 sea-water is 0.504 V versus saturated calomel electrode (SCE), compared with -0.726 V for hydrogen evolution. The corresponding high potential implies that the battery voltage will be significantly higher than that of the batteries which rely on hydrogen evolution as the cathodic reaction. Though both the oxygen reduction and hydrogen evolution produce OH^- which alkalisies the cathode surface, the degree of alkalisiation of the surface by oxygen reduction is far less than in the case of hydrogen-evolution cathode operating at 10 mA cm^{-2} , since the limiting current for oxygen reduction is likely to be $\sim 0.5 \text{ mA cm}^{-2}$. This should reduce the rate of precipitate build-up on the surface and part of it may be dissolved more readily since the movement of sea-water will moderate the pH of the solution near the surface of the electrodes.

Aluminium alloy anodes

Aluminium as an anode is attractive because of its very negative potential and electrochemical equivalence and availability. However, it is subject to a high overpotential in use which is thought to be due to the formation of passive deposits on the surface of the electrode [7]. Aluminium alloys with superactive discharge characteristics in alkaline batteries have been developed and they exhibit a potential that is approximately 700 mV more negative than structural alloys [8]. Alcan International Laboratories of Banbury, UK, supplied their newly developed aluminium alloy, AB50V, for this study. This alloy contains 0.63% Mg, 0.14% Sn, 0.04% Ga and 0.0018% Fe. Figure 1 shows the steady-state polarisation curve of this alloy in 3% NaCl solution at room temperature. The open-circuit potential of this alloy is about -1.45 V versus SCE which is significantly better than the normal Al alloys ($\sim -1.1 \text{ V}$ for AlZ2).

Improved cathode catalysts

Early work on corrosion batteries for military and biomedical applications have relied on the use of Pt black cathodes, since cost is of secondary importance. For sub-sea applications, cost must be minimised. The traditional way of reducing the cost

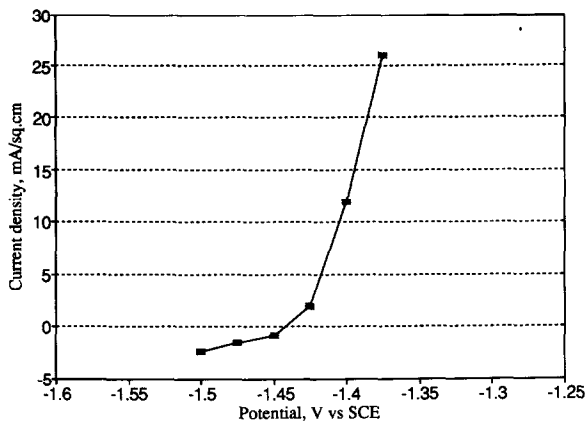


Fig. 1. Steady-state polarisation curve of an AB50V Al alloy in 3% NaCl solution at room temperature.

of precious metal cathode is to use Pt/C catalysts. By dispersing ultrafine Pt particles ($\sim 100 \text{ \AA}$) on high surface area C supports, the utilisation of available Pt is significantly improved. However, since the current density of an Al battery operating with hydrogen-evolving cathode is at the most $\sim 10 \text{ mA cm}^{-2}$, even at a loading of 1 mg Pt cm^{-2} , the cost is still too high. Previous work has shown that it is possible to reduce the Pt content in the catalyst by means of WO_3 as the active support instead of C. The evolution of hydrogen can be extended to the WO_3 surface via the formation of the conducting H_xWO_3 . Very high activity could be achieved at very low Pt loadings in acidic media [9, 10]. It should be noted that the Pt/ WO_3 electrode used in previous work was based on the impregnation of chloroplatinic acid on WO_3 , followed by freeze-drying and vacuum decomposition at $300 \text{ }^\circ\text{C}$ for 1 h. This preparation method would only disperse Pt particles on WO_3 particles and the spillover reaction is limited to sites where there is Pt/ WO_3 particle contact and the utilisation of Pt is not high. Recently, we prepared Pt/ WO_3 electrodes using coelectrodeposition from a solution containing chloroplatinic acid and dissolved tungsten and showed that Pt is very well dispersed in the WO_3 matrix [11]. Tests of a $0.2 \text{ mg Pt/WO}_3 \text{ cm}^{-2}$ hydrogen-evolution cathodes in 3% NaCl solution showed that the performance is comparable with a Pt/C cathode containing 1 mg Pt cm^{-2} . However, on testing the Pt/ WO_3 hydrogen-evolution cathode at 10 mA cm^{-2} in artificial sea-water, the performance of the battery deteriorated after 10 h due to the accumulation of hydroxide deposits on the surface of the electrodes. The relatively high current density will lead to a rapid increase in the pH of the solution near the electrodes, leading to the precipitation of hydroxide sludge.

Much higher battery voltages can be achieved if dissolved oxygen is used as the oxidant. Moreover, the changes in pH of the solution will be minimal because of the low operating current density. In this case, inexpensive, non-noble metal catalysts for oxygen reduction have to be used. In this work, we concentrated our studies on the Teflon-bonded $\text{Co}_3\text{O}_4/\text{C}$ cathodes, since previous work by Tseung and coworkers [12] has shown such electrodes possess very good performance in alkaline solutions.

Figure 2 shows the performance of a Teflon-bonded $\text{Co}_3\text{O}_4/\text{C}$ electrode operating at 0.1 mA cm^{-2} in artificial sea-water and the performance is similar to that of a Teflon-bonded Pt/C (Pt loading: 0.4 mg cm^{-2}) oxygen-reduction cathode.

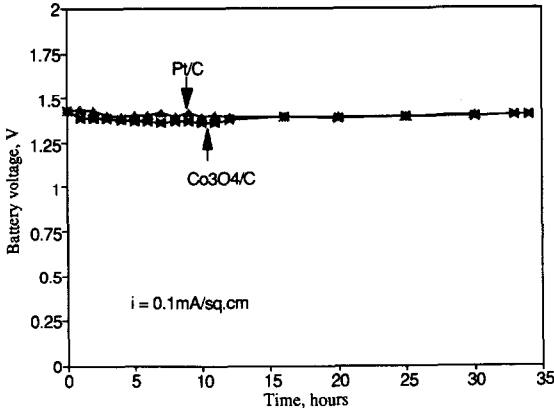


Fig. 2. The performance of a Teflon-bonded $\text{Co}_3\text{O}_4/\text{C}$ and a Pt/C ($\text{Pt}=0.4 \text{ mg cm}^{-2}$) cathode operating at 0.1 mA cm^{-2} in artificial sea-water.

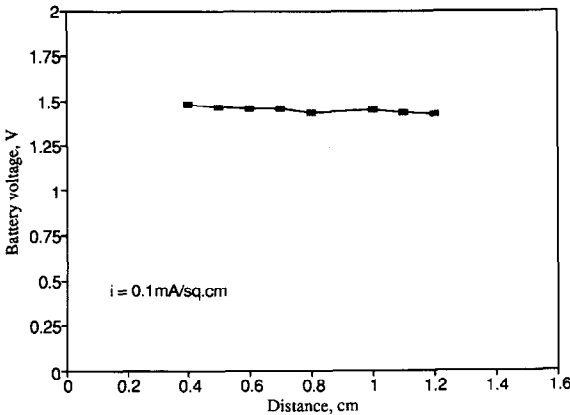


Fig. 3. The effect of anode/cathode gap on the battery voltage in 3% NaCl solution at 14°C .

Battery development

For long-term operations in sub-sea environments, Al/water batteries using oxygen-reduction cathode should overcome the following problems:

(i) Prevention of marine growth and the formation of hydroxide or calcareous layers at the electrodes.

(ii) Minimum increase in IR losses due to the dissolution of the anode.

The effect of anode/cathode gap on battery performance operating with oxygen-reduction cathode (mode 2) is given in Fig. 3. There is no significant change in performance by varying the anode/cathode gap from 0.4 to 1.2 cm. In addition, when the design is based on an anode with a cathode on either side, the results suggest that even 20 cm thick anode could be used without any worries about the increase in IR losses with time. Since the resistivity of sea-water is typically $25 \Omega \text{ cm}$ [13], the IR loss is only 25 mV for a 10 cm gap under the operating current density of 0.1 mA cm^{-2} .

(iii) Minimising of the self-discharge of anode. All active anode materials will react with water thus reducing faradaic efficiency. Therefore, it is important to reduce the amount of anode surface exposed to the sea-water to a minimum.

Evaluation of long-term performance in sub-sea environment

Installation of the underwater test facility

Three batteries were installed side by side. The surface areas of both anode and cathode for each battery are 1 cm^2 . A cube of AB50V Al alloy was used as anode material and the cathode was a Teflon-bonded Pt/C (Pt loading: 0.4 mg cm^{-2}) electrode. The anode/cathode gap was fixed at 0.5 cm. The batteries were bolted to a Dexion box and the electrical leads and resistive loads were housed in a junction box bolted at the top of a mooring pole in Brightlingsea Harbour, Essex. The Dexion frame was bolted to the bottom of the pole and the clearance between the bottom of the sea bed and the frame was about 60 cm. This is to ensure that the batteries will still be immersed in sea-water at the low tide. After installation, the first measurement showed that the performance was almost the same as laboratory test in 3% NaCl solution. However, there was significant decrease in performance with time. The whole test assembly was lifted out of the water after 80 days and examined. The anode/cathode gap was gummed up with mud and whitish deposit (hydroxides). There was, however, no evidence of any biological or marine growth on either the anode or the cathode. One possible explanation is that the aluminium anode surface is continuously changing because of dissolution, and no growth is possible. In the case of the Teflon-bonded cathode, since Teflon is non wetting, the likelihood of marine growth is greatly reduced. In addition, the increase in pH at the cathode is not conducive to the growth of marine organisms.

Installation of the second test rig in a floating pontoon

In order to avoid the clogging of the anode/cathode gap by mud, the second test rig was installed in a floating pontoon further away from the shore. The test assembly was assembled about 30 cm below the water surface and the assembly was about 120 cm from the bottom at low tide.

Figure 4 shows all three batteries maintained stable output $\sim 1.4 \text{ V}$ (0.1 mA cm^{-2}) over a test period of 21 days, significantly better than the results obtained in the first trial.

Sea trials of the third test rig using Teflon-bonded $\text{Co}_3\text{O}_4/\text{C}$ cathodes

The third test rig was commissioned and two sets of batteries were tested. These batteries were made with Teflon-bonded $\text{Co}_3\text{O}_4/\text{C}$ cathodes. The results shown in Fig. 5 are obtained from a set of batteries with the anode/cathode gap of 0.5 cm. Figure 6 shows the results of another set of batteries which had a gap of 2 cm between the anode and the cathode. There was hardly any difference in output between the two sets of batteries up to 50 days, again confirming that at lower current densities, the effect of IR losses due to the distance between two electrodes are low enough to be of insignificant consequence. Postmortem examination of the first set of batteries after 100 days revealed that the electrodes were covered with the whitish brown deposits, indicating the inclusion of mud particles with the hydroxide precipitates. The high coverage of the electrode surface by the deposits results in the decrease of the battery performance. On the other hand, though there was some precipitate on the

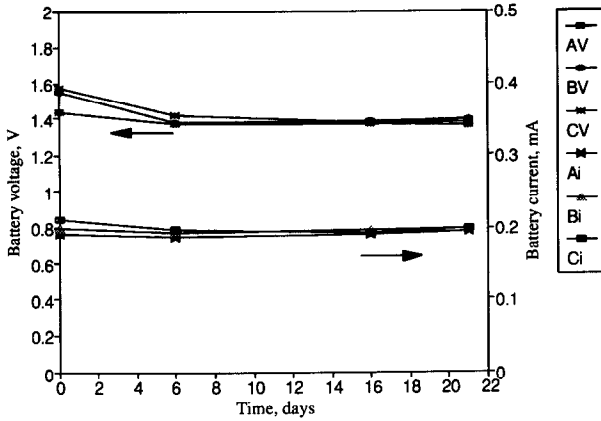


Fig. 4. The changes in battery voltage and current with time. Test site: floating pontoon, Teflon-bonded Pt/C cathode. AV, BV and CV are the voltages of batteries A, B and C, respectively, and Ai, Bi and Ci are the currents.

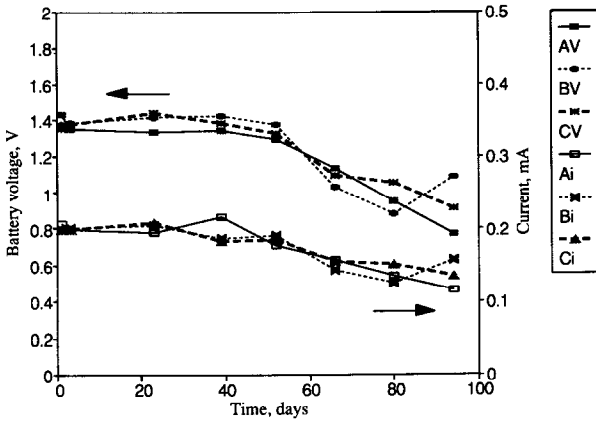


Fig. 5. The changes in battery voltage and current with time. Test site: floating pontoon, Teflon-bonded $\text{Co}_3\text{O}_4/\text{C}$ cathode, anode/cathode gap: 0.5 cm. AV, BV and CV are the voltages of batteries A, B and C, respectively, and Ai, Bi and Ci are the currents.

surface of the electrodes in the second set of batteries after a test period of 70 days, it was far less serious than the first set of batteries, suggesting that the greater separation between the anode and the cathode enables the hydroxide precipitates to flow away from the batteries more readily.

Discussion and conclusions

The reason for choosing special Al alloy from Alcan International Ltd. for most of this work is because of their lower self-discharge rate, compared with the Mg alloys [14]. However, it may be better to consider the use of Mg alloys as anodes in the light of the results of the sea trials. The fact that we are getting $\text{Al}(\text{OH})_3/\text{mud}$ deposits

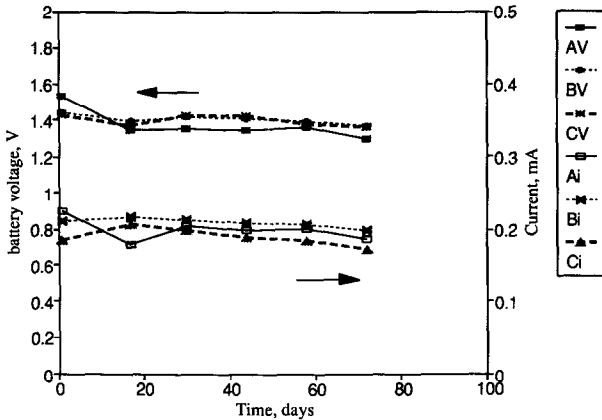


Fig. 6. The changes in battery voltage and current with time. Test site: floating pontoon, Teflon-bonded $\text{Co}_3\text{O}_4/\text{C}$ cathode, anode/cathode gap: 2 cm. AV, BV and CV are the voltages of batteries A, B and C, respectively, and Ai, Bi and Ci are the currents.

on the electrodes in sea trials is not surprising since the solubility product, K_{sp} , of $\text{Al}(\text{OH})_3$ is 1.3×10^{-33} . However, the solubility product of $\text{Mg}(\text{OH})_2$ is only 1.8×10^{-11} . In other words, the anodic reaction product of Mg is significantly more soluble than that of $\text{Al}(\text{OH})_3$ and will therefore be less likely to form precipitates on the electrode surface.

Teflon-bonded $\text{Co}_3\text{O}_4/\text{C}$ oxygen-reduction cathodes have proved to be almost as active as Pt/C catalysts (Fig. 2) at low current densities. Moreover, test up to 120 days in sea trials have shown that they are not poisoned and that there is no growth of marine life on the surface. This could be due to two reasons: (i) the presence of polytetrafluoroethylene (PTFE) on the electrode surface, making it difficult for the marine life to attach onto the surface, and (ii) increase in pH of the solution at the surface of the electrode due to oxygen reduction. High pH solution is not a suitable media for the growth of marine life.

The energy density for such a corrosion battery is higher than that of best primary lithium battery. One method of improving the current output from such batteries is using many parallel cathodes on each side of the anode. It is known that the current output is limited by the oxygen reduction on the cathode. However, the current can be increased by increasing the cathode area. Since the cathodes are porous, there is adequate electrolyte pathway between each cathode layer. The use of such multi-cathode battery will significantly increase the current output but without causing significant changes in the pH at the cathode surface, thus avoiding the precipitation of $\text{Ca}/\text{Mg}(\text{OH})_2$. Moreover, the higher power output from each battery will greatly decrease the parasitic loss from the self-discharge of the anode, since the total exposed area of the anode remains the same. Figure 7 shows the performance of a 1 cm^2 Al alloy anode/5-cathode battery. The battery output was 0.5 mA cm^{-2} for anode and the performance is the same as the one with the current density at 0.1 mA cm^{-2} .

In the conceptual design of a 25 W multi-cathode Al/water battery, it is assumed that the operating current density is 0.2 mA cm^{-2} for each cathode and the operating voltage is 1.3 V. By using $\sim 1 \text{ m}^2$ Al anode and $5 \times 1 \text{ m}^2$ cathode on either side of the anode, the amount of Al alloy used in 1 year is:

$$W = (ItN)/F \quad (4)$$

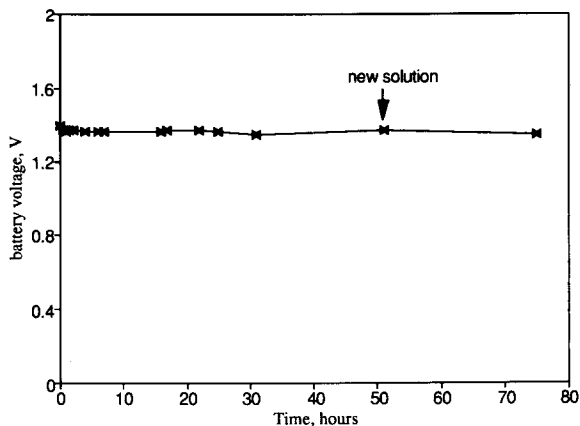


Fig. 7. Voltage vs. time curve of an Al/5 cathode battery in 3% NaCl solution (0.5 mA cm^{-2}).

where I is operating current, t operating time, N the electrochemical equivalent of Al, and the F is Faraday constant. The calculated weight of Al, including 30% self-discharge, is $\sim 74 \text{ kg}$. The weight of 10 cathodes is estimated to be 50 kg and the weight of current collectors, reinforcing structures, etc., is estimated to be 50 kg. The total dry weight of battery is 174 kg. This results in an energy density of 1260 Wh kg^{-1} . It is important to note that the energy density of best primary lithium battery is 500 Wh kg^{-1} [1]. On the other hand, the battery voltage can be readily increased to 15 V by a d.c. to d.c. converter [15]. This device can start at 0.7 V and the output limit with $\sim 80\%$ efficiency. The use of such a converter will only reduce the energy density of the Al/multi-cathode battery to 1008 Wh kg^{-1} .

Further sea trials on offshore facilities over longer periods are necessary before these batteries would be commercialised.

Acknowledgements

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