

Developing a Battery Using Set Concrete as Electrolyte

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This paper presents a brief account of a developing electrochemical power source which uses set concrete (in this case, set cement paste containing no aggregate) as electrolyte. The system is designed with an aluminium anode which dissolves during discharge, and employs reduction of water to hydrogen on steel as cathode. The system functions as an alkaline aluminium/water cell, and can be operated at low current density.

Introduction

The need for remote power sources in remote areas such as applications in deep sea oil wells and pipelines is a challenge to be met. A primary battery source using dissolving aluminium as the anode is potentially possible, but requires careful thought for reactions of the cathode. Since deep sea conditions have very little dissolved oxygen, reduction of oxygen as the cathodic reaction is impossible. This eliminates any possibility of a metal/air battery system. Most primary batteries which use anodic oxidation of aluminium as the anodic reaction employ reduction of oxygen from air as the cathode (the so-called aluminium/air cell), and considerable single-cell voltages have been achieved. In these aluminium/air batteries, it is conventional to use either highly alkaline electrolytes, such as KOH of high concentration, or to use fairly concentrated chloride solutions, of approximately neutral pH. The essence of these electrolytes, particularly the alkaline ones, is that they are pure, with only known additives to improve performance. Much research has been carried out on these systems (1-13). The aluminium/air battery is otherwise similar to the zinc/air battery, which has found commercial application.

In the deep sea condition, the aluminium anode must function in a similar way, but the question of the cathode still arises. Some suggestions have been put forward in the past, such as reduction of ferricyanide (10) and reduction of hydrogen peroxide (11-13). The latter has even been formed into a microcell battery using platinum as the cathodic electrocatalyst (13). These systems, which show considerable performance by using a high-potential cathodic reaction. However, they would require injection of further cathodic reactant as that reactant is consumed, if they are to operate for a long period of time. A remote power source should avoid this, and that fact has suggested the notion of simple reduction of water to hydrogen as the cathodic reaction. What should also be borne in mind for long-term operation, even at low loads, is the fact that the anode materials (aluminium in this case) are thermodynamically unstable in water (14), even when there is no load. Nevertheless, there is a potential application for an electrochemical cell, based on aluminium dissolution as anodic reaction, and reduction of water as cathodic reaction. The system would be analogous to the aluminium/air cell, but with small output voltage because of the lower-potential cathodic reaction. This paper

explores some aspects of the development of a primary electrochemical cell which uses aluminium oxidation as the anodic reaction, and the reduction of water to hydrogen as the cathodic reaction.

The present work examines some aspects of the possibility of setting up an electrochemical cell using aluminium as the anode and set concrete as the electrolyte. With steel acting as the cathode electrocatalyst for the reduction of water to hydrogen, the system aims towards setting up a battery system in a deep-sea oil well, where the well consists of a steel pipe surrounded by concrete. The concrete separates the steel pipe from the surrounding rock. The characteristic for this system is a very low oxygen content: the cathodic reaction cannot be reduction of oxygen under these circumstances.

Note that although set concrete is a solid electrolyte, it is probably true that most of the ion conductance in the electrolyte is via pore water. Pore water in concrete accounts for much of its electrolytic properties (see eg. 15-20): the solid components are probably extremely resistive. The pore water of concrete contains a saturated solution of cement compounds, with a high area-to-volume ratio within the network.

Experimental Method

The experiments described here were carried out in order to define the characteristics of anodic dissolution of aluminium as the anodic reaction, with set concrete as electrolyte, and reduction of water to hydrogen on steel as the cathodic reaction. Because of the resistivity of set concrete, such a system could operate only at low current density. Instead of concrete, which contains aggregates, we tested cement paste, made with cement and water only. No aggregates were employed in the solid electrolyte phase.

Electrochemical polarisation

Experiments consisted of measuring polarisation curves of aluminium in cement slurry and in 0.02 M calcium hydroxide solution. The aluminium used here was of purity 99.999%. Curves were measured potentiostatically, using the period required to allow the metal to reach an approximate steady state at each potential. Each potential was measured starting with the lowest value first, allowing it to reach an approximate steady state current, and then incrementing the potential to the next value. This method was applied between the potential limits of -2 V(SCE) and -1 V(SCE). The cell used was of capacity *ca.* 0.75 dm^3 , and was deaerated thoroughly before and during use. The cell was also equipped with a platinum counter electrode and a Haber-Luggin capillary probe linked by an electrolyte-filled tube to an externally mounted reference cell. The reference cell contained the same electrolyte as the working cell. The connecting tube was of length *ca.* 30 cm, and was used to prevent contamination of the working cell by chloride anions. It also ensured that the cell was kept free of mercury. A saturated calomel reference electrode (SCE) was used for these experiments, and all electrode potentials in this paper are referred to the SCE. These measurements were performed in deaerated electrolytes, whose oxygen content was minimised by purging with white-spot nitrogen.

Experiments with the cathode were performed with pure iron, of purity 99.5% or 99.975%. These experiments involved measurements of the cathodic reduction of water to hydrogen, using the same systems and cells as described above for the anodic reaction.

Working electrodes were in each case made from a cylinder of diameter 5 mm for aluminium, and 10 mm for iron, each mounted with epoxy resin into a specially designed holder made of polymethyl methacrylate. These electrode holders were threaded in the back to hold a steel shaft from which electrical contact to the outside circuit was made. The rear side was completely isolated from the electrolyte. A single circular surface formed the working electrode of each sample.

In each case electrode surfaces were prepared to a constant surface finish by the following procedure. The surfaces were first wet-ground to 600 grit, then cleaned ultrasonically, then wet-ground to 1200 grit, then cleaned ultrasonically, and finally washed thorough. The water used through all grinding and cleaning procedures had been distilled twice.

Chemicals used, apart from the cement itself, were all of analytical grade. The electrolytes were made using twice-distilled water. Electrolytes used were alkaline. Set concrete and cement paste have pH between 12.5 and 13.5, and the system was designed to simulate or emulate these conditions.

Measurements on single cells

Apart from the electrochemical measurements on individual electrodes, measurements were also carried out on single aluminium/concrete/water cells, using pure Al as anode, and iron as cathode, both set into concrete. The cells were cast inside tubes made of reinforced polyvinyl chloride of wall thickness 5.5 mm. The cell electrodes were either of area 11.42 cm² or 5.0 cm², each pair of electrodes mounted symmetrically with respect to the other. These were set in a cement paste made of cement and twice-distilled water, using water-to-cement ratios of 0.4 to 0.5.

These experiments were designed to test aluminium/concrete/water cells in the absence of oxygen. The experiments were therefore conducted in a large hooded chamber of internal capacity *ca.* 0.4 m³. The chamber was sealed from the external environment apart from gas inlet and outlet ports. The gas inlet was fed from an external cylinder with white-spot nitrogen, whose role was to deaerate the chamber thoroughly. Throughout testing, the chamber was fed continuously with nitrogen. Only when the nitrogen source cylinder had to be replaced by a fresh one, did the oxygen content of the chamber rise a little. The total oxygen within the chamber was monitored with a Mettler-Toledo oxygen transmitter. The oxygen probe was sited in the chamber atmosphere, and not in the cement paste samples. With this equipment, we were able to lower the oxygen content in the atmosphere of the test chamber to *ca.* 5 parts per billion (ppb).

The cells were polarised at low current density using an external polarising source. For simplicity, this was done galvanostatically using a home-built source as a discharge device. The device allowed for polarisation of five specimens simultaneously, with the cell voltage being read from digital voltmeters in the equipment. The wiring to these was fed via a sealed, gas-tight electrical connector through the wall of the test chamber. When installed, readings were taken from the cells approximately every 15 minutes for the first 6 hours, and then approximately every 60 min for the daylight hours. Gaps in the readings occurred over night time periods. The polarisation of these single cells was continuous for periods up to 28 days. The purpose of this was to test not only the performance of the cells, but importantly also the stability of the cells under defined load.

The temperature of all experiments reported here was ambient, at 291 ± 3 K.

Results and Discussion

Polarisation of pure aluminium in alkaline electrolyte is shown in Figure 1. The result demonstrates that aluminium does dissolve anodically in dilute alkaline solution, but the current densities are not very high. This essentially defines the maximum theoretical rate at which an aluminium anode might be expected to oxidise in cement systems. Note that in the anodic region, the current rises to a plateau and becomes approximately independent of potential. This is indicative of the presence of a surface film. The measurements shown in Figure 1 are in an approximate steady state, and this is therefore the steady-state anodic dissolution rate of the metal. By virtue of the independence of the rate on potential, it is apparent that dissolution of aluminium occurs through a surface oxide film, which must effectively remain intact. The metal cannot however, be regarded as passive, since the rate of anodic dissolution in the plateau region is too high. Note too, that this could be indicative of a useful discharge characteristic of the metal when acting as the cell anode, provided the discharge current is kept low. The form of Figure 1 implies that if the current density drawn through the cell is kept low, the aluminium should be hardly polarised, and the cell would fail if attempts were made to draw a discharge current density larger than the plateau current density. We can deduce from this system that aluminium will function as a low-current density anode in electrolytes of this nature, but the current density capable of being drawn from the system is low.

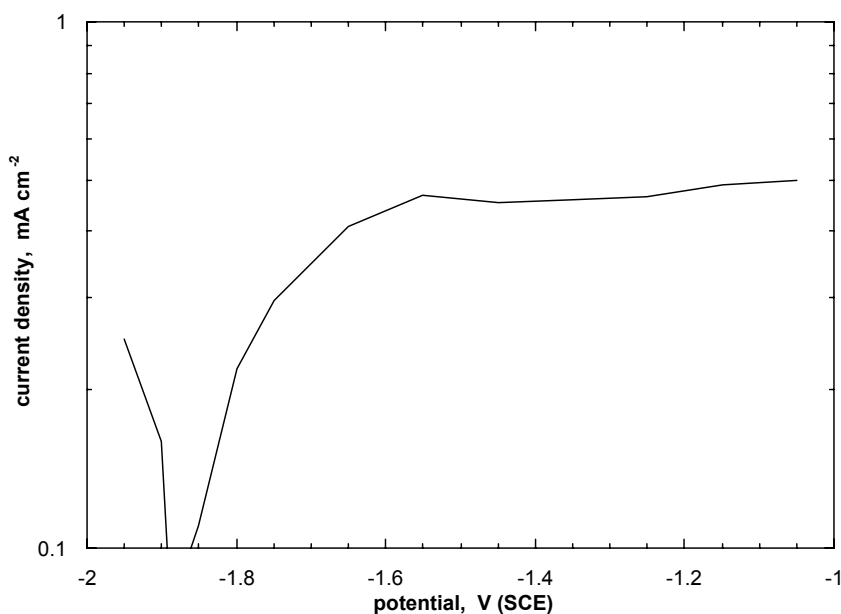


Figure 1. Polarisation of pure aluminium in 0.02 M calcium hydroxide solution at ambient temperature. The current densities are approximately steady state.

Figure 2 shows the behaviour of aluminium in the cement slurry. This slurry was made using a water-to-cement ratio of 7.5. Its characteristic was a solution of cement compounds, and a residual solid phase which did not dissolve throughout the course of the experiments. The form of the data is the same.

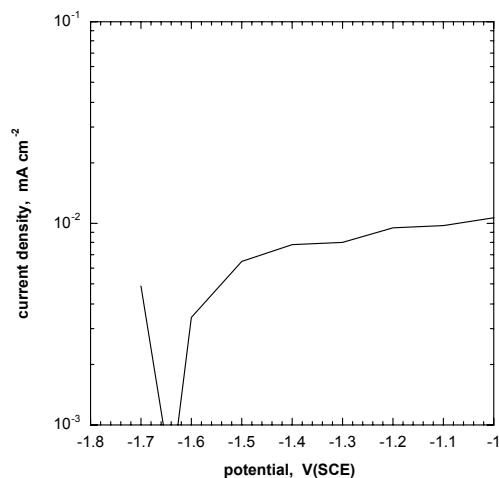


Figure 2. Polarisation of pure aluminium in cement slurry at ambient temperature. Slurry formed with a water-to-cement ratio of 7.5.

The current rises to a plateau value, and shows little polarisation if the current density is small. However, the plateau current density displayed is considerably lower than that shown by the simple aqueous electrolyte in Figure 1. Aqueous cement slurry is a poorer electrolyte than the pure alkaline solution for the battery system investigated.

In Figure 3 is plotted a set of data from a single cell polarised at a constant current density of 250 nA/cm^2 . Only the last 150 h of testing are shown. On the same plot is a simultaneously measured oxygen concentration. There is much variation in the cell voltage, over a range of about 1 V. This appears to be due to the variation in the oxygen content of the test chamber, since the voltage varies roughly synchronously with the variation in the oxygen content.

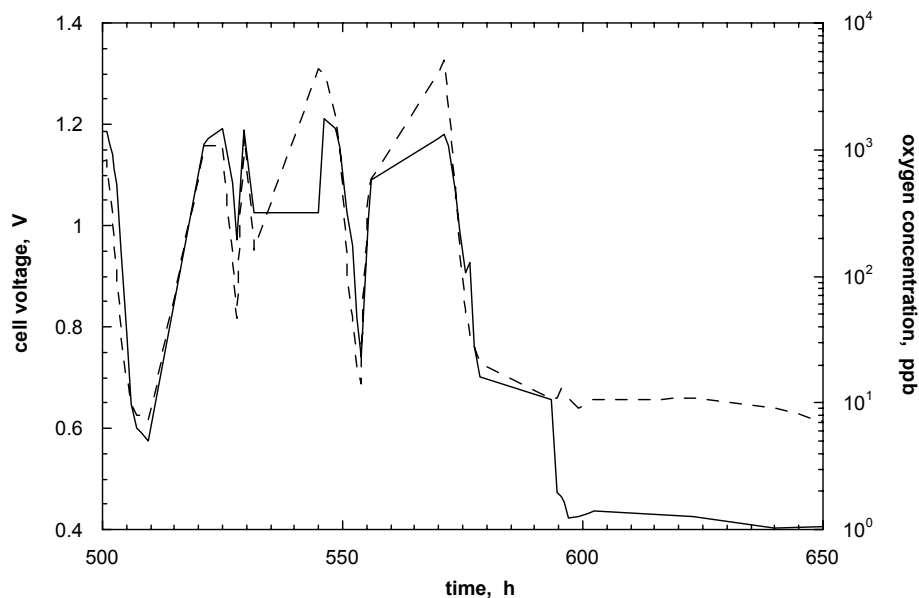


Figure 3. Discharge characteristics of an aluminium/cement paste/water single cell discharged at 250 nA/cm^2 (solid line, left-hand ordinate). The cathode on which water was reduced to hydrogen was pure iron. The broken line is the corresponding oxygen concentration in the test chamber measured simultaneously (right-hand ordinate). The graph shows only 150 h of behaviour between 500 and 650 h of continuous discharge. The solid cement paste electrolyte was made with a water-to-cement ratio of 0.5.

This particular cell gave an operating voltage of 0.4 V, giving a power output of 100 nW cm^{-2} . The cells were particularly sensitive to the oxygen concentration, with an operating voltage of $> 1 \text{ V}$ if the oxygen concentration was high. In this case, the cell was then functioning as an aluminium air cell. The reasons for the higher oxygen content were two-fold. Some of these were necessary incursions of air when the gas supply cylinder needed changing. Other parts of the graph, which showed high oxygen concentrations and high cell voltages, were effected deliberately in order to test the effect of oxygen.

The system was tested with varying water-to-cement ratio. It was initially thought that increasing the water-to-cement ratio beyond that which is normally regarded as the minimum required to hydrate all the cement would raise the porosity and thereby also the permeability of the cement paste, allowing bigger current density to follow with lower electrolyte resistance. However, this improvement was not observed. Surprisingly, the effect was to demonstrate that raising the water-to-cement ratio too far gave a poorer operating voltage, as demonstrated in Figure 4.

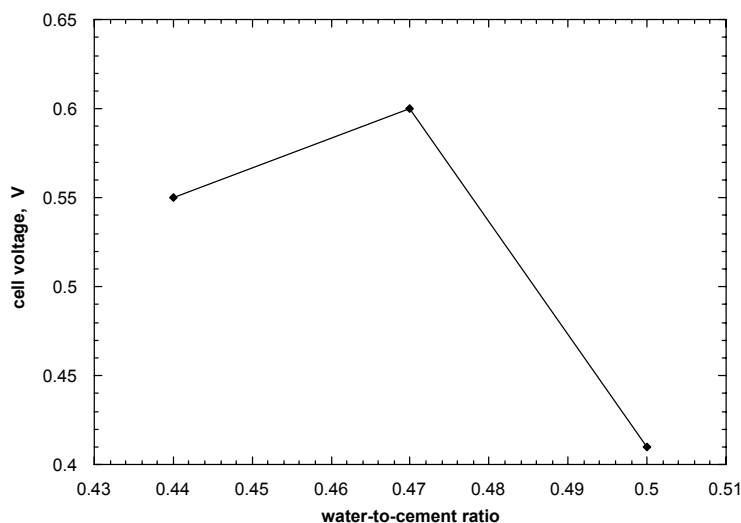


Figure 4. Output voltage of aluminium/cement paste/water cell under galvanostatic load of 250 nA/cm^2 as a function of the water-to-cement ratio in the cement paste. The data shown were observed at the end of a test period of 28 days continuous discharge. The cathode was pure iron giving cathodic reduction of water to hydrogen. The oxygen content was low in each case.

The highest voltage recorded here was 0.6 V, recorded for a cell with a water-to-cement ratio of 0.47. Although rather few water-to-cement ratios were used as shown in

Figure 4, the data show that the output voltage under load was extremely sensitive to this aspect of the cement paste mix. What emerges from this is the fact that the output of this battery is quite sensitive to the detailed constitution of the cement paste. This important point will be addressed in other work.

Note that the cathodic reaction is hydrogen evolution on the steel surface. For successful operation of such a battery system, the evolved hydrogen must be able to be dissipated away from the steel surface at a rate commensurate with the rate at which it is produced. If this were not the case, then the evolved hydrogen would build up pressure at the steel/cement interface. Since the electrolyte is a solid, this would result in cracking of the brittle electrolyte, and in hydrogen permeation of the steel. Hydrogen permeating into steel also embrittles the steel, with possible crack formation. This battery system could therefore be used only under low discharge current *density*. Significant current (ie absolute current, not current density) can nevertheless be drawn in principle by using a large surface area for the battery system. This large surface area is in any case required to allow reasonable ion current (absolute current) to flow through the electrolyte.

We tried using zinc and magnesium as anode materials, but they did not perform as well as the present system. The zinc anode responded quite well to the alkaline solutions to give dissolution current densities which were comparable with those of aluminium. However, the potential of the zinc anode under load is considerably higher (more positive) than that of the aluminium anode, and that must inevitably lead to lower voltages and lower power densities if such a battery system were under load. This can in fact already be seen from the equilibrium thermodynamics of the metal/water systems given by Pourbaix (14). The difference in equilibrium potential between the Zn/ZnO electrode and the H₂O/H₂ electrode is *ca.* 0.4 V, and that is the maximum theoretical voltage from such a cell, prior to any polarisation. For aluminium, the corresponding difference in equilibrium potentials is *ca.* 1.5 V.

The problem with magnesium tested in similar conditions was different. The Mg/Mg(OH)₂ electrode has a very low equilibrium potential, even lower than that of aluminium, and this was not the barrier. What makes the Mg electrode difficult to use in these circumstances is the fact that the metal is quite passive in alkaline solution, probably because the oxide MgO has low solubility at high pH. A very passive anode cannot provide the current output required of such a battery system. Of the three metal anodes tested, aluminium was by far the most successful. Note that all three of these metals (Al, Zn and Mg) are used successfully as sacrificial anodes in cathodic protection, but the main use is in corrosion protection in sea-water environments. In sea-water electrolytes, the chloride anion acts as depassivating agent to allow the anode to dissolve at a controlled rate. In cement paste, the alkaline nature of the electrolyte acts to dissolve aluminium and zinc anodically, but not magnesium.

Conclusion

A low power battery can be constructed which employs set concrete as electrolyte, and which can be used in the absence of oxygen. In this battery, a dissolving aluminium anode is supported by reduction of water to hydrogen on steel as the cathodic reaction. In the absence of chloride in the electrolyte, aluminium can be made to dissolve anodically

into the alkaline electrolyte at a low but steady rate. Zinc and magnesium are not suitable anodes for this system.

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