

Development of a seawater battery for deep-water applications

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Abstract

Dissolved-oxygen seawater batteries rely on the corrosion of a reactive metal anode and the reduction of oxygen at an inert cathode to generate a potential of about 1 V when immersed in seawater. Because oxygen is not very soluble in seawater, such batteries are characterized by small cathodic current densities and are therefore most suitable for long-term low-power applications. A number of batteries have been built recently using sophisticated electrodes. The objective of this study was to evaluate the feasibility of building a seawater battery using cheap readily-available materials. The results show that magnesium anodes outperform aluminum. Although the cathodic current densities achieved in this study are markedly lower than reported previously, cathodes composed of copper (or stainless-steel) mesh perform reasonably well and facilitate the design of compact batteries with an open structure and large cathodic areas. Deep- and shallow-water tests show that a battery occupying 1 m³ could produce 5 W for a year or more in oxygen-saturated waters and 1–2 W in the oxygen-starved waters of the North Pacific seafloor. The energy density of such a battery including the flotation necessary for optimal performance and recovery is estimated to be 150–400 Wh kg⁻¹.

Keywords: Seawater batteries; Anodes; Magnesium; Aluminum

1. Introduction

Within the oceanographic research community, time-series measurements in deep waters are frequently obtained with self-contained instruments anchored to the seafloor. Such devices can be deployed and recovered remotely from a surface vessel by including flotation and a releasable anchor. Recent advances in low-power electronics and data storage devices have resulted in considerable improvements in deployment periods and capabilities. Often the power requirements for even long-term experiments can be met straightforwardly with conventional primary lithium or alkaline cells contained within the pressure case holding the electronics. However, for some applications the battery pack is sufficiently large that it must be housed in a separate pressure case. If this is to be recovered with the electronics, additional flotation must be added which increases the instrument bulk and costs. Alternatively, the battery pack may be abandoned on the seafloor with the anchor, but this also increases the costs since the pressure cases must be replaced. From an economic standpoint, the high power density of lithium cells is offset by their high cost, and neither lithium or alkaline batteries are particularly attractive power sources once the energy requirements exceed ~1 W-year.

Seawater batteries are potentially an alternative power source for long-term low-power instruments. They rely on the corrosion of a reactive metal anode in seawater and the reduction of oxygen or water at an inert cathode to generate an electrochemical potential of about 1 V. Because seawater is the electrolyte, the electrodes are not housed in a pressure case and the power density is potentially very high. Modern field-effect transistors (FETs) facilitate the construction of efficient power inverters which can be used to convert the cell potential to a useful voltage. If necessary, a seawater battery can trickle charge a small secondary cell to supply bursts of concentrated power.

The concept of slow-discharge seawater batteries is not new; several designs were patented [1,2] and the US Navy funded substantial early development work, the results of which are apparently unpublished. In the past few years seawater batteries have been the subject of renewed interest [3–10] and research has focused on the use of catalyzed cathodes to enhance current densities [3,4,6,7,10] and specialized anode alloys to increase cell voltages and minimize self-discharge [3,7,10]. Several sophisticated batteries have been developed for military and commercial applications. Although high power densities are always desirable because they minimize instrument bulk and hence, simplify deployments and recoveries, the primary criterion which determines

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the choice of power sources within the academic community is generally cost. The objective of this study was to investigate the feasibility of constructing, with commonly available materials, a cheap reliable seawater battery for use in the deep oceans.

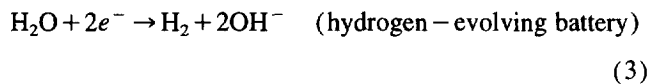
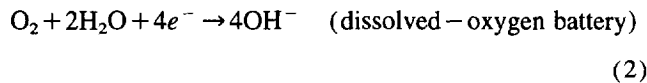
2. Electrochemistry

The electrochemical reactions for a seawater battery can be written in their simplest form:

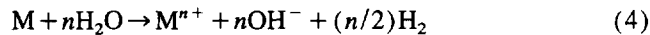
(i) anode



(ii) cathode



where M represents a reactive metal of valence n . The most suitable choices are aluminum and magnesium. In addition to the current generating reactions, the anode will undergo hydrogen-evolving corrosion



The importance of this self-discharge reaction can be minimized by reducing the surface area of the anode, but magnesium anodes are not practical in warm waters because the corrosion rates are too high.

The highest operating potentials are obtained when dissolved oxygen is reduced at the cathode. However, oxygen has a low solubility in seawater and the maximum current is limited by the diffusion of oxygen to the cathode. Dissolved-oxygen batteries must be built with a large open cathodes and compact batteries are limited to a few watts. Hydrogen-evolving batteries operate at a lower voltage but can, in principle, support much higher current densities. However, because they operate at high loads, a very small electrode separation must be maintained to minimize the internal resistance [11]. At high current densities, the alkalinity generated by the cathodic reactions can lead to the precipitation of insoluble salts of magnesium and calcium which are detrimental to battery performance. For these reasons, all the large-scale seawater batteries built to date have utilized dissolved-oxygen cathodes and we limited this investigation to such batteries.

3. A comparison of electrode materials

The first part of our study was a comparison of several small test batteries constructed with magnesium and 6061 aluminum alloy anodes and graphite, copper, and 316 stainless-steel cathodes. Each battery was constructed from two

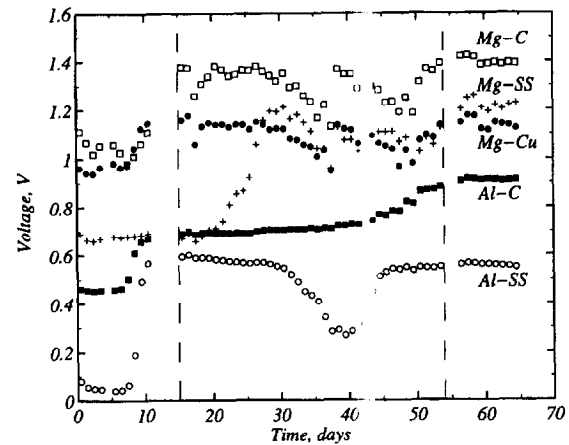


Fig. 1. Voltage vs. time plots for shallow-water tests of five small batteries constructed with magnesium (Mg) and 6061 aluminum alloy (Al) anodes and graphite (C), copper (Cu), and 316 stainless-steel (SS) cathodes. The tests were conducted in 10 m of water in Puget Sound. Each battery comprised two vertical electrode plates measuring 30 cm \times 15 cm, spaced 4 cm apart, and connected by a 50 Ω resistor. Voltages have been averaged over 24-h periods. For most of the test the batteries were located on the seafloor. Vertical dashed lines delineate short periods at the start and end of the tests when the batteries were floated at mid-water depths.

vertical electrode plates measuring 30 cm \times 15 cm which were spaced 4 cm apart and connected by a 50 Ω resistor. The batteries were deployed for 65 days in Puget Sound during March to May 1995, in 10 m of well-oxygenated seawater at 8 $^{\circ}$ C [12]. For most of the test, the batteries sat on the rocky seafloor although near the start and end they were floated at mid-water depths. With the exception of two short periods, the battery voltages were logged every half hour. The test results are summarized in Fig. 1 and Table 1.

The flow of seawater over the cathode improves battery performance because it thins the boundary layer for oxygen diffusion. At our deployment site, sea currents are primarily tidal and normally do not exceed about 0.1 m s $^{-1}$. Nevertheless, these currents were sufficient to produce significant short-term fluctuations in the cell voltages when the batteries were deployed on the seafloor. When the batteries were floated below a jetty, 54 days into the deployment, wave agitation stabilized the voltages although tidal fluctuations were still evident. The voltages displayed in Fig. 1 have been averaged over 24-h periods.

The most prominent feature common to each battery is a sharp increase in the cell voltages which occurs over a period of 2 to 10 days, 1 to 3 weeks into the deployment. The increase was particularly large for batteries constructed with stainless-steel cathodes. This effect has been reported elsewhere [4,6] and is the result of the formation of a beneficial biological layer on the cathode. A second small voltage increase observed on the aluminum-graphite battery after about 45 days of operation and a temporary decrease in the voltages of the aluminum-stainless-steel battery after 40 days may also have biological causes.

All the test batteries operated at current densities that are several times lower than typical values of 1 A m $^{-2}$ reported for catalyzed cathodes [3,4,6,7,10]. Magnesium anodes gen-

Table 1
Performance of small test batteries

Electrodes		Days 0–5			Days 55–65			
Anode	Cathode	Voltage (V)	Power (mW)	Current density ($A\ m^{-2}$)	Voltage (V)	Power (mW)	Current density ($A\ m^{-2}$)	Faradic efficiency (%)
Mg	SS	0.67	9	0.14	1.22	30	0.26	13
Al	SS	0.06	0.1	0.01	0.56	6	0.12	60
Mg	Cu	0.95	18	0.20	1.14	26	0.25	12
Mg	C	1.06	23	0.23	1.40	39	0.30	14
Al	C	0.45	4	0.10	0.91	17	0.20	35

Each battery comprised two 30 cm × 15 cm electrode plates spaced 4 cm apart and connected by a 50 Ω resistance. Faradic efficiencies for aluminum cathodes are an upper bound because an oxide layer formed on the electrode during the test.

erate higher potentials than aluminum. The only drawback of magnesium is a lower Faradic efficiency, a consequence of higher rates of self-discharge. The best performance was obtained for the magnesium–graphite battery. At the end of the deployment, the magnesium–stainless-steel battery slightly outperformed the magnesium–copper battery, although the latter was markedly better before biological layers formed.

4. A prototype battery assembly

For the second part of this study we constructed two identical prototype assemblies, one for further shallow-water testing and one for a deep-water deployment. Each assembly (Fig. 2) consists of both a magnesium–graphite and a magnesium–copper battery sharing a common anode and a logging device to monitor performance. A cylindrical magnesium anode is surrounded by 8 radiating graphite plates and an outer screen of copper mesh which in addition to acting as the second cathode, protects the brittle graphite. The electrodes are 30 cm high and are sandwiched between Plexiglas sheets. An external resistance and a simple logging device are housed in a small pressure case attached to the top of the assembly. The total exposed areas of graphite and copper are 1.05 and 0.8 m², respectively. When deployed in seawater,

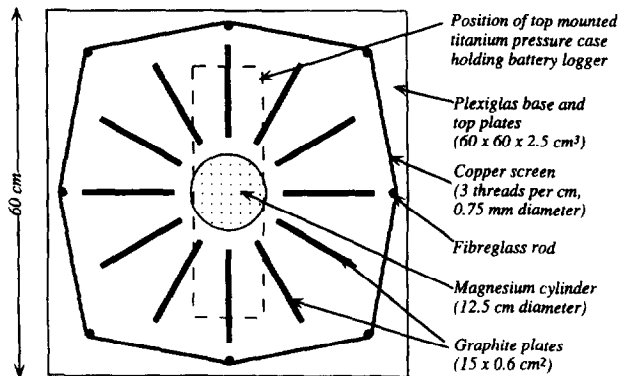


Fig. 2. Plan view showing the mechanical configuration of the prototype seawater battery used for shallow- and deep-water tests. The dashed box shows the position of a top-mounted pressure case holding the battery logger.

the internal resistance is about 0.25 Ω for the magnesium–copper battery and is considerably less for the magnesium–graphite battery.

The shallow-water testing was conducted over 8 months between July 1995 and March 1996. Here we present results obtained well after the formation of beneficial biological layers and in the winter when the waters are saturated with oxygen (8 ml/l) [12]. The batteries operated with seven different load resistances and Fig. 3 shows the average voltage and power per unit area of cathode as a function of the load which is also normalized to the cathode surface area. Except at the two highest resistances where the operating voltages were very steady, the voltages have been averaged over at least a week to eliminate tidal fluctuations. For both batteries, the highest powers are obtained at relatively high

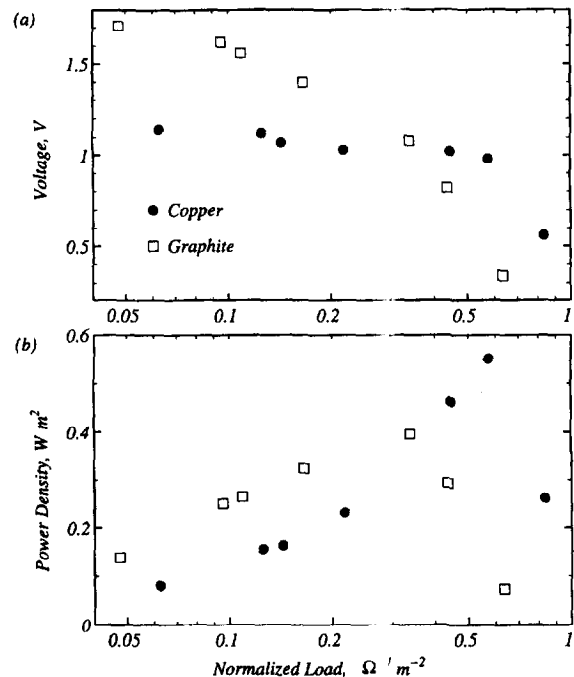


Fig. 3. (a) Voltage and (b) power density as a function of load normalized to the cathode surface area for magnesium–copper and magnesium–graphite batteries floated at mid-water depths in 10 m of water in Puget Sound. Except for the two lowest loads, each measurement has been averaged over at least 1 week to minimize the effects of tidal current induced fluctuations.

loads for which cathode current densities reach about 0.5 A m^{-2} . At normalized loads exceeding $0.4 \Omega^{-1} \text{ m}^{-2}$, the magnesium–copper battery outperforms the magnesium–graphite battery. Our tests do not demonstrate any fundamental difference in the performance versus load properties of the two cathode materials because the difference in the voltage curves is most simply explained by the more exposed position of the copper electrodes on the exterior of the assembly (Fig. 2). However, for practical reasons, the robust nature of the copper screen makes a more open design practical. Over six months of testing the combined Faradic efficiency of the batteries was nearly 70%.

The deep-water test was conducted in the summer of 1995 in the NE Pacific near 48°N , 129°W . The assembly was deployed by submersible on the seafloor at 2200 m depth, where the temperature is 4°C [13], for a period of 100 days; each battery operated at a fixed load resistance of 5Ω . At a given depth, oxygen concentrations in the North Pacific are the lowest found in the open oceans [13]. At our site the oxygen concentration (1.7 ml/l) [13] is only 22% of saturation at atmospheric pressure. As for the shallow-water tests, there is a strong correlation between the battery voltages and sea currents (Fig. 4(a)) which were measured 50 m above the seafloor less than 500 m away from the battery. Even after smoothing with a 24-h running mean, the voltage curves for the whole deployment (Fig. 4(b)) show significant fluctuations. For the magnesium–graphite battery, the voltage curve

is characterized by an 0.15 V increase after 30 days followed by a gradual increase of about 0.1 V over 40 days. Both of these features are probably a consequence of beneficial biological activity. However, biological effects are less apparent for the magnesium–copper battery. For the first part of the deployment the magnesium–copper battery voltage significantly exceeds that of the magnesium–graphite battery, but following a sudden decrease of 0.15 V in the potential of both batteries after 50 days, the voltages curves moved towards one another. For the last 30 days, they track each other fairly closely although the magnesium–graphite battery displays larger short-term fluctuations. The combined Faradic efficiency of the batteries was 30%.

In retrospect, it is clear from the characteristics of the voltage curves that the operating load was higher than the optimal value for the relatively low oxygen concentrations found at our deep-water site. When compared with the shallow-water tests, the battery performance may also have been adversely affected by the lower temperatures (4°C as opposed to 8°C). The average power normalized to the cathode surface area was 0.06 W and 0.14 W m^{-2} for the magnesium–graphite and magnesium–copper batteries, respectively. The power output for the magnesium–copper battery decreased from 0.17 to 0.11 W m^{-2} during the second half of the deployment for reasons that are unclear. The close correspondence of the voltage curves during the last 30 days suggests that the potential of the two batteries was coupled in some manner. However, we can see no reason for this and the recording electronics were functioning normally when the battery was recovered. The degradation in performance of the magnesium–copper battery may be a consequence of operating the battery at too high a load.

5. Discussion

Our tests show that magnesium is a better choice than aluminum for the anode of a cold-water dissolved-oxygen battery. In our test, the Faradic efficiency of pure magnesium anodes increased from about 13 to nearly 70% as the average current density at the anode increased from about 0.2 to over 5 W m^{-2} . Previous work also shows that a Faradic efficiency of $\sim 60\%$ can be achieved at large anodic current densities [6] and self-discharge can also be minimized by alloying the magnesium with aluminum [7]. Although pure-graphite cathodes operate at a higher open-circuit potential than copper or stainless steel, they are probably not practical for a battery deployed from a surface ship because they are too brittle. Our tests show that it is very important to design a seawater battery with a very open structure in order maximize the advection of oxygen towards the cathode. Copper and stainless-steel meshes are readily available and are ideal cathode materials since they facilitate the construction of compact but open cathodes with a very large surface area. In our shallow-water tests, stainless-steel cathodes slightly outperformed copper after the formation a beneficial biological

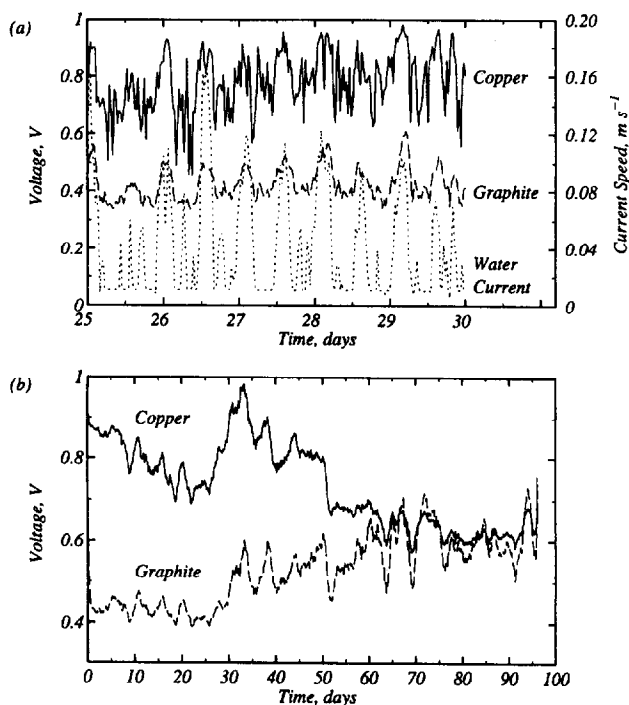


Fig. 4. Results of the deep-water test on the seafloor of the North Pacific at 2200 m depth. (a) Unsmoothed data for a 5-day period showing the strong correlation between magnesium–copper (solid) and magnesium–graphite (dashed) battery voltages and water currents (dotted). Water currents were measured at 2175 m depth less than 500 m from the seawater battery (data courtesy of R.E. Thomson, Institute of Ocean Sciences, BC, Canada). (b) Voltages smoothed with a 24-h running mean for the full deployment.

layer, 1 to 3 weeks into the deployment. However, for most applications a battery must perform at full power soon after deployment and the test at 2200 m depth showed no clear evidence for the formation of a beneficial biological layer on a copper cathode.

By incorporating a cathode composed of wire mesh, it is possible to design a 1 m³ battery with a negligible internal resistance and a cathode surface area of ~ 10 m². We estimate that such a battery would generate about 5 W in oxygenated surface waters and 1–2 W in the poorly oxygenated waters found on the seafloor of the North Pacific. The shallow-water tests also suggest that performance may improve significantly if the battery is floated above the seafloor. We have designed and tested a simple power inverter which can boost the cell voltage to 14 V. At 1 V the inverter operates at 80–85% efficiency and a small central processing unit (CPU) could be incorporated to adjust the load to maximize the power output. Assuming that the battery electronics and a small secondary holding cell are housed within a pressure case containing other electronics and that the anodic efficiency is 40% (a figure which accounts for both self-discharge and losses in the power inverter), we estimate that the energy density would range from 200 Wh kg⁻¹ for a 1-W 1-year battery to 500 Wh kg⁻¹ for a 5-W 2-year battery. If flotation is incorporated the energy density decreases to 150–400 Wh kg⁻¹. While these energy densities are lower than values of 500–1000 Wh kg⁻¹ reported for more sophisticated seawater batteries [3–7,9,10], they are comparable with the energy densities of primary lithium (450 Wh kg⁻¹) and alkaline cells (150 Wh kg⁻¹), even when pressure cases and flotation required for such cells are excluded. A seawater battery could be constructed cheaply and because the mechanical configuration is simple and the electronic components in the power inverter need operate at only small fraction of their capacity, it should also be very reliable.

Acknowledgements

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