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CHARACTERISTICS OF AN IMPROVED INERT-CATHODE/ MAGNESIUM-ANODE SEA-WATER BATTERY

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ABSTRACT

The inert-cathode/Mg-anode sea-water battery has demonstrated the capability to furnish power, generally in conjunction with a dc-dc converter, for a variety of marine underwater devices. A battery of this sort may be tailored to application and its performance predicted to within 10 to 20% of actual. The focal point for the design process is the cell-voltage/current-density characteristic, which varies with electrode materials and conditions of use. The variations of this characteristic and its dependence on conditions of use are essentially circumscribed in this discussion.

Shelf life is long, upward from several years, on the basis of experience and materials. This shelf life presumes storage without the electrolyte and refrigeration. One exception exists in the case of the impulse cell where exposed storage periods in the order of 1 year lessens the magnitude and rate of cell response upon activation and the energy supplied over a given interval. Such loss may generally be compensated by initially allowing a greater margin of power. Operating life is adversely affected by accumulations of reaction products and varies with electrode spacing and current density. More than 60 days of continuous operation have been achieved at the reduced current density of about 1 ampere per square foot.

Series-battery terminal voltages of about 1.5 volts are conveniently achieved in the interests of compactness and converter efficiency. Higher voltages in series systems are achieved with greater cell isolation.

PROBLEM STATUS

This is an interim report on one phase of the problem; work is continuing on other phases of the problem.

AUTHORIZATION

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CHARACTERISTICS OF AN IMPROVED INERT-CATHODE/MAGNESIUM-ANODE SEA-WATER BATTERY

BACKGROUND

In 1959 and 1961 reports from the Lincoln Laboratory (1) and the A.D. Little Co., Inc. (2), cited the potential for the inert-cathode/Mg-anode cell as an economical long-life, low-power source for underwater ASW surveillance systems. The principal problems then recognized were the cell clogging from insoluble reaction products and low cell voltage. Previous work on the inert-cathode cell dated back many years but had been given little formal documentation. The high cathode polarization effects and the consequent low cell voltage placed it at a disadvantage in comparison to other batteries with respect to practical application. The advent of better catalytic agents for the cathode, however, did promote increased interest in the midfifties and later (3-5).

The motivation to explore anew the possibilities of the inert-cathode cell for marine-based electrical supplies generated from a newly developed NRL tunnel diode converter (6), which operated from voltages in the 0.2 to 0.55 volt range, squarely straddling the output range of the sea-water cell. This converter development had proceeded on the premise that greater reliability could be realized from sources as thermoelectric, thermionic, solar cell, and fuel cell, if their output voltages could be transformed to usable levels with a minimum of series connections of unit cells. This approach would minimize the total number of parts to the overall electric source–inclusive of the tunnel diode converter, the number of connections, and insulators under high-temperature stress–or the amount of interconnecting conductors and fuel lines, and, hence, at least theoretically improve overall reliability. Since the practical realization of the then new electrical sources was slow in coming, attention was turned to the sea-water cell as a possible source with which the tunnel diode converter could first be used.

Subsequent development of the battery/converter combination satisfied the electrical requirements for a steadily increasing number of sea-water-based equipments, notably ASW sonobuoys and emergency rescue devices. Further gains in longevity of cell operating duration indicate promise for naval mines. The converter introduces filtering and stabilization which virtually eliminates electrical noise produced when voltage fluctuations are created by battery gassing. Finally, the surprisingly high momentary energy release on initial activation has met a wide variety of needs in the field of sea-water-activated squib-firing devices with far greater ready-for-use life and economy than previously known.

VOLTAGE-CURRENT CHARACTERISTICS

Representative Characteristics

The characteristics shown in Fig. 1 are representative of the cell performance per unit area that may be expected of the inert-cathode/Mg-anode system discussed here. They circumscribe a performance range achievable with commonly available materials and may be used as the basis for design to specific requirements. But several constraints in their use must be recognized. A given voltage-current characteristic relates to a corresponding set of conditions: type of cathode construction and configuration, surface treatment, type of Mg-anode alloy and anode configuration, sea-water electrolyte composition and conditions, interelectrode spacing, and overall battery configuration. The curves

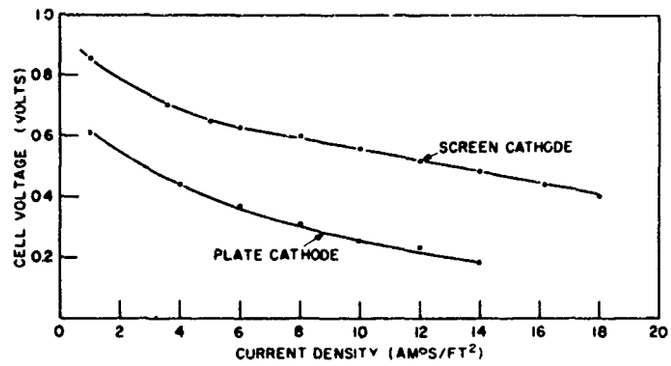


Fig. 1 - Voltage-current characteristics for an inert-cathode/Mg-anode sea-water cell. The anode is Mg (AZ-31B plate), and the cathode is a steel sheet or screen (double 8 mesh) with Ni and Pd plating. The electrolyte is artificial sea water with a conductivity of 52 millimhos at 22°C. The spacing within the cell is 1/8 inch, and the specimen size is 2 by 4 inches.

of Fig. 1 apply to simulated sea water at a temperature environment of 22°C and approximately sea-level pressure. When used as a basis for the design of a specific battery of all parallel cells, they have consistently produced results within 10 to 20% over that experienced in actual battery test. Their predictive role in series battery design is another matter. In this latter instance, the series-connected cells operate in a common electrolyte. As a result, intercellular leakage currents generally produce a condition whereby the battery terminal voltage is less than that estimated on the basis of summing all voltages indicated by the voltage-current characteristic. The situation of a series connection of cells in a common electrolyte will be expanded later.

Returning for a moment to the disparity between predicted and measured results, the further consideration arises on the dropoff of voltage during operation. These reductions are somewhat greater per unit of time than conventional batteries experiencing equivalent operation. (This is a situation, however, for which the companion converter may readily compensate.) As a result, the average lifetime voltage of an actual battery is less than that predicted by the laboratory-determined voltage-current characteristic, because the latter is measured in a relatively stabilized state 15 to 30 minutes after activation. This disparity will vary with current density, operating life, electrolyte conditions, and battery materials and configuration. Figure 2 illustrates the typical dropoff in the voltage-current characteristic with operation for high current densities. For a given cell load resistance the resultant locus of operating points describe a line through the origin, with a slope equal to the value of the load resistance. This type of voltage variation for operation at lower current densities is shown later in connection with long-term operation.

Temperature and Salinity Effects

The voltage-current characteristics of Fig. 3 are representative of the effects of temperature at constant salinity. Salinity is defined here as the amount in grams of solid material dissolved in one kilogram of sea water, usually written as S ‰. Through knowledge of the variation in conductivity of sea water with temperature and salinity (7), it can be shown that the performance changes illustrated in Fig. 3 are due principally to electrolyte conductivity changes. In fact, an equivalent circuit model serves to account for effects

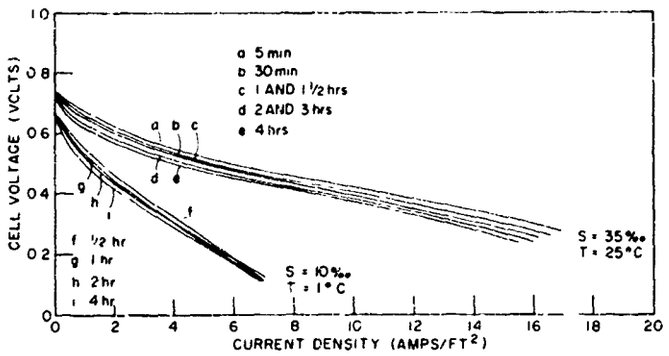


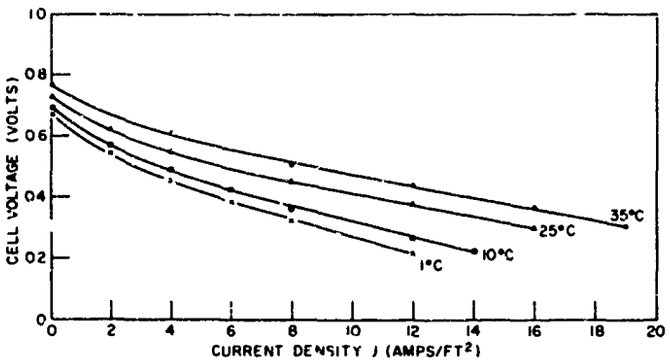
Fig. 2 - Variation of the cell performance over a 4-hour operating interval at high-current-density operation. The loading is approximately 16 amperes/square foot over operating intervals between voltage-current density measurements. The spacing within the cell is 1/8 inch, and the specimen size is 2 by 4 inches. The anode is Mg (AZ-31 plate), and the cathode is a 36-by-40-mesh screen with Ni and Pd plating. The lower series of curves represents a salinity of 10 ‰ and a temperature of 1°C; the upper series of curves represents a salinity of 35 ‰ and a temperature of 25°C.

of temperature variations to within 2 to 15% of confirmatory measured values. Specifically, the equivalent circuit internal voltage may be approximated by the ordinate intercept of the slope line tangential to the characteristic at a given current density. At a given current, the internal voltage drop, i.e., the difference between internal and terminal voltages, may be adjusted according to the ratios of electrolyte conductivities for the temperatures in question (7). A similar procedure would apply for calculating effects of salinity changes. This model neglects the effects of temperature on the electrode polarization potentials.

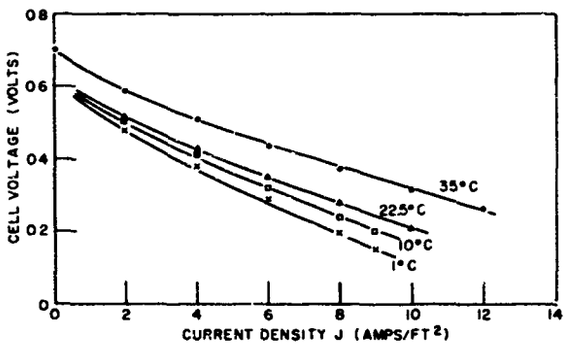
OPERATING LONGEVITY

Although the factors which bear on the protracted operation of this type of inert-cathode/Mg-anode system are known qualitatively, the quantitative extent to which they, in concert, affect performance cannot be predicted. Among the factors that bear most directly on long-term operation are current density; spacing and electrolyte circulation; electrolyte conditions, such as pH, amount of dissolved CO_2, salinity, and microorganism content; cathode texture; anode efficiency; and completeness of anode corrosion. It has proven most expedient to resort to experiment in assessing the extent to which these combined influences bear on cell operating life. The results discussed below disclose that conditions can be controlled to a significant extent in prolonging life. In general, clogging must be avoided, and electrode scale or film formation must remain sufficiently pervious to ion flow. In studies to date, the limiting of current densities, promoting efflux of electrolyte-bearing insoluble particles, and use of screen cathodes have proven most instrumental toward achieving long-life operation.

Some results of improved long-life cell operation are shown in Fig. 4. The use of screen cathodes not only enhances power output but results in a lesser tendency toward clogging of the intercellular space. The disparity in overall shape between the 1/8-inch



(a) Constant salinity of 35 ‰



(b) Constant salinity of 10 ‰

Fig. 3 - Effect of temperature variation on voltage-current characteristics. The anode is Mg(AZ-31 plate), and the cathode is a 36-by-40-mesh screen with Ni and Pd plating. The spacing within the cell is 1/8 inch, and the specimen size is 2 by 4 inches.

anode curves and the 1/4-inch anode curves is due to Mg-plate warpage, which was essentially prevented in the case of the 1/4-inch anode cells.

Figure 4 shows that the longest operating was slightly greater than 60 days. The resultant energy density was 167 watt-hours per pound on a dry-cell basis for the 50-day result. Anode efficiency was approximately 62% for the actual amount of Mg consumed. Due to the nonuniform wearout observed, the effective anode efficiency was 39%, based on the total available Mg. Figure 5 shows the so-called worn-out anode, which actually is only used up 65% by weight. Needless to say, the use of this remaining Mg is a goal now being pursued.

A further point should be considered for purposes of practical design. The curves of Fig. 4 indicate voltage levels of about 0.4 volt at less than 1-ampere/square-foot current density, whereas the curves of Fig. 1 indicate voltages in the 0.6 to 0.8 volt region at this

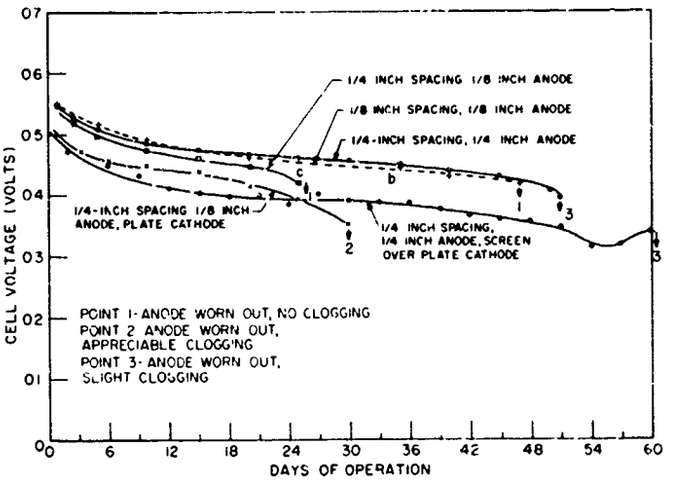


Fig. 4 - Results of long-term cell operation. The salinity is 35 ‰, and the temperature is 22°C. The specimen size is 12 by 12 inches. The cell is Mg(AZ-31); the cell cathode is a 12-by-14-mesh screen with Ni and Pd plating; the cell load is 0.64 ohm.

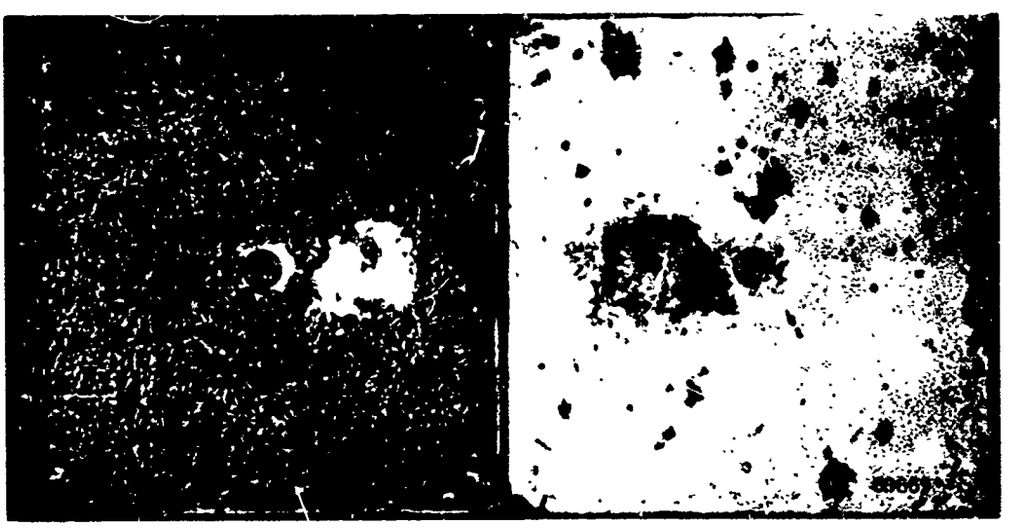


Fig. 5 - Worn-out anode

current density. This situation is characteristic of long-term operation at the lower current densities, for reasons akin to those discussed in connection with the variation of cell performance over the operating interval (Fig. 2). At the higher current densities, however, the greater anodic and cathodic actions contribute to electrolyte turbulence and flushing through hydrogen production and sloughing mechanisms, as well as to local temperature elevation. These factors contribute to the lessening of design predictability cited earlier.

OPERATION IN THE OPEN OCEAN AS COMPARED WITH LABORATORY OPERATION

The data presented in Fig. 6 indicate that this type of Mg-anode/inert-cathode system will operate satisfactorily in an actual oceanic environment. Although such tests are only a first step in establishing feasibility for ocean operation, they show that reaction products are not deleterious in excess of those experienced in the laboratory for periods up to about 2 weeks. Imminent ocean trials will expand these results for correlation over the 60-day or greater periods, corresponding to the long-term laboratory results discussed previously. Biological or microbiological fouling, not encountered in the laboratory or 2-week sea trial, may arise to affect long-term performance. Inspection of Fig. 6 shows the necessity to maintain a spacing of 1/8 inch or greater for operating periods of this duration, i.e., days to weeks.

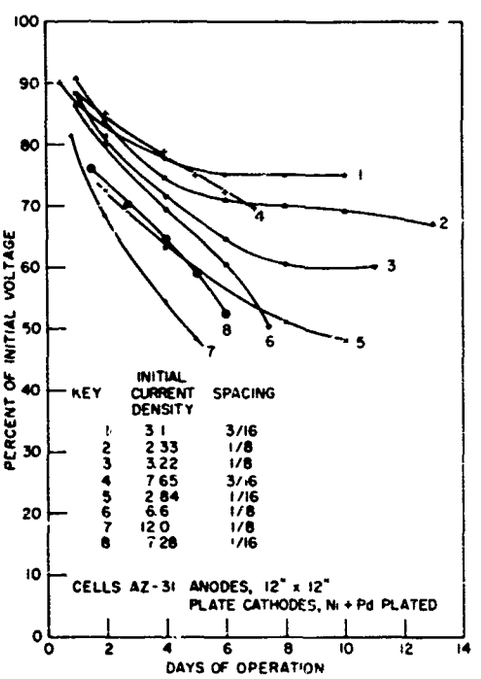


Fig. 6 - Ocean tests at various current densities and spacing. The specimen size is 12 by 12 inches. The anode is Mg (AZ-31), and the cathode is Ni and Pd plated.

The curves of Fig. 7 indicate that results experienced in laboratory operation are representative of those encountered in the open ocean. The ocean tests were performed in 190 feet of water at Argus Island, 25 miles southwest of Bermuda. Cells tested in the ocean indicate a lesser tendency for clogging, due most probably to a greater flow of fresh electrolyte.

With regard to the tradeoff between power output level and current level, in plate-type cathode versions, observation of the test results shows that clogging will not occur at 3.0 to 3.5 amperes/square foot for spacings at or greater than 1/8 inch for these operating durations. Larger spacing appears to offer gains toward achieving higher power output for a clog-free operation but this incurs the penalty of greater electrolyte resistance drop. This drop is particularly undesirable with respect to cold-temperature operation, as well as the widening gap upon anode wear.

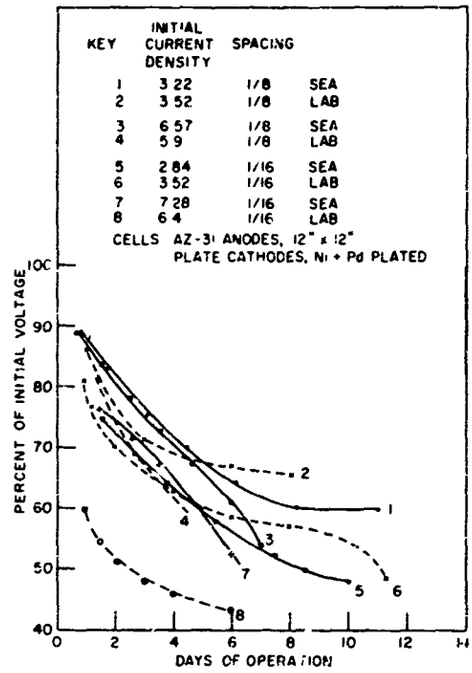


Fig. 7 - Comparative results of ocean and laboratory tests. The specimen size, cathode, and anode are the same as specified in Fig. 6.

SERIES SYSTEMS

The problem of placing cells, such as those under discussion here, in series in a common electrolyte reduces to one of achieving electrical isolation or insulation among cells, yet observing sufficient openness of interelectrode spaces to prevent clogging. Accomplishing both conditions simultaneously calls for excessively large batteries, or unreasonably small values of watts per unit volume. Again compromise or tradeoff is called for whereby reasonable isolation is achieved with little or no restriction in interelectrode-space electrolyte ventilation. From the foregoing discussion, it is apparent that any battery configuration of these inert-cathode/Mg-anode cells must not significantly reduce electrolyte access and reaction product efflux from that indicated for the simple open cell. These circumstances, then, lead to the practical expedient of keeping any resultant battery voltage at levels below roughly the 12-volt level. For the lower powers, in the order of watts or tens of watts, it has proven convenient to attain only a sufficiently high voltage, say 1.5 to 3.0 volts, which will permit efficient and economical use of a transistorized converter coupled to the battery. At higher power levels, say hundreds of watts, the 3.0 to 6.0 volt level appears practicable per battery section with sections isolated and placed in series to produce 12 volts. A transistorized or SCR converter should then process this 12-volt power for electronic loads.

The approach to fabrication of series batteries treated here involves placing sides on rectangular-shaped electrodes, thus isolating cells from any leakage in the side regions. The top remains open for gas escape along with that for some of the insoluble floculent products of reaction. The open bottom allows gravity-induced escape of heavier concentrations of reaction products plus electrode sloughing. To achieve cell isolation at the top and bottom, so-called barriers are placed between cells, extending an arbitrary length above and below the battery.

The determination of proper extension lengths for these barriers has been the subject of both experimental and analytical study, the former only being reported here. The

analytical study solves the electrostatic problem for a system of parallel plates at different potentials. This solution leads to a determination of leakage currents and from these leakage currents the net battery terminal voltage. Taken from experimental results, Fig. 8 shows the effect in fine scale of barrier length on a three-cell series batteries. At this level the leakage tendency is relatively small, but 1-inch extensions will produce about 4% gain in voltage. Figure 9 shows the comparative effects of end barriers at the 1.5, 3.0, 4.0, and 6.0 volt levels. The increasing severity of leakage with voltage level is apparent.

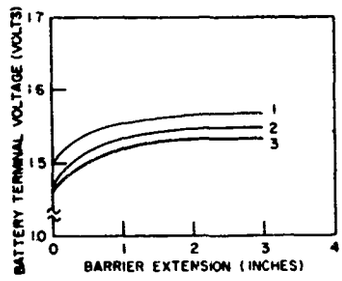


Fig. 8 - Effect of end barriers at the 1.5-volt level. The specimen size is 2 by 4 inches. The anode is Mg (AZ-31), and the cathode is plated sheet steel. Cells 1, 2, and 3 are identical.

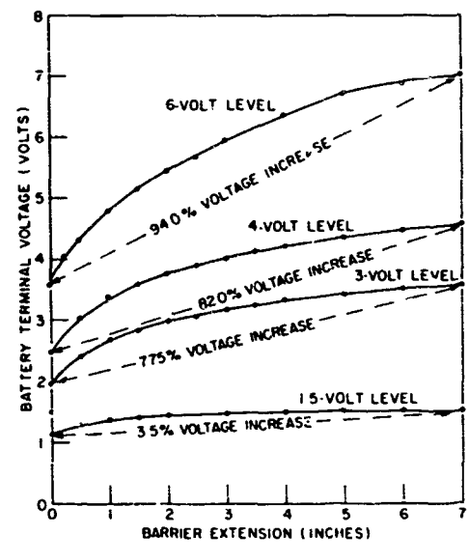


Fig. 9 - Effect of end barriers in series batteries at various voltage levels

The results shown in Fig. 9 may be compared in terms of the change in voltage as barrier length is varied from 0 to 7 inches.

Operation at the 1.5-volt level takes on added significance from the results above in that it is the least demanding on barrier length, which, of course, augurs well for compactness. This gain is to be added to that for the attendant converter, which at the 1.5-v level can operate efficiently and with low-cost transistors. The use of larger barriers results in a relatively lesser size penalty as the power level and concomitant electrode dimensions are increased. As power is increased at a given voltage, the barrier extension length remains unchanged for a desired barrier effect, since it deals with what are essentially end effects or external leakages.

IMPULSE BATTERIES

The initial activation of these cells is invariably accompanied by a terminal voltage which in the first several seconds following activation may be more than 100% above the subsequent steady-state value. The effect persists strongly for as much as 10 to 15 seconds. That is, after 10 to 15 seconds the voltage may yet be 60 to 75% above a later 1-hour or steady-state value, depending on the battery load resistance, age, and previous environmental history, and materials plus construction. It is thought to be due to momentary depolarization of the cathode by surface oxides and/or dissolved oxygen in the electrolyte. For those special applications requiring triggering energy upon activation with sea water, the inert-cathode/Mg-anode cell has demonstrated adequate energy storage capacity to fire explosive squibs, which in turn power a subsequent mechanical or hydraulic actuation mechanism. Equally important to the needs at hand is the ability to retain this capability over months of exposed ready-to-use standby or storage.

Although cells of this type are intrinsically more resistant to exposed storage deterioration than the silver chloride type of sea-water battery, they are not impervious to aging. The particular aging of concern here is the reduction in ability to supply energy quickly upon activation. Surface contamination could be of a nature as to inhibit electrochemical action and quick impulse response for a period of seconds or minutes, yet eventually clear away for good steady-state performance. The impulse cell is more sensitive to aging than the longer term cells.

To gain some notion of the effect of exposed aging on impulse action, quantities of batteries were placed in both controlled and exposed environments, and samples were withdrawn periodically for measurement and recording of voltage and energy to a specified load. The results of the energy measurements are shown in Fig. 10. Since one important application requirement for these cells called for squib firing within a 3-second interval after immersion, the energy points apply solely to the 3-second time following activation. The recorded data from which these points are taken, however, include energy (i.e., integrated power) and instantaneous voltage up to several minutes. From this more general data picture, it was observed that over a 5 to 10 second interval energy output always exceeded requirements. The straight lines of Fig. 10 approximate the lower bounds of 3-second energy for both storage conditions.

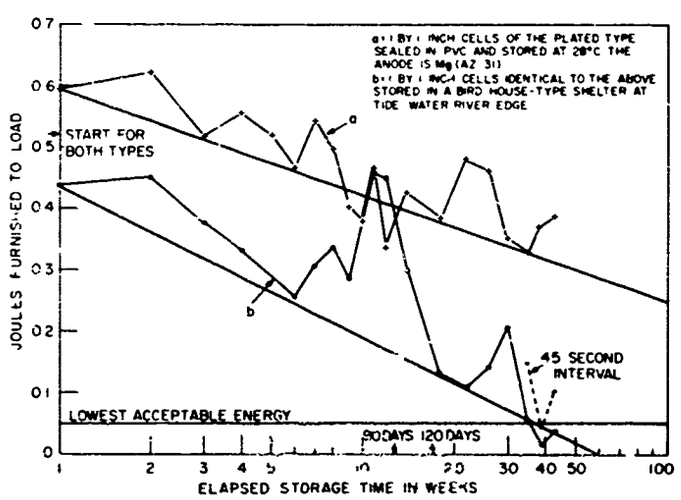


Fig. 10 - Impulse battery performance. The energy was released into a 3-ohm load during a 3-second interval.

The curves of Fig. 11, especially the curve characterized by an exposed environment, illustrate the manner in which the impulse battery responds after aging. The delay of the exposed cell in achieving peak voltage is clearly shown in direct contrast to the immediate rise demonstrated by the cell which had been kept in a PVC sealed package prior to activation. The corresponding energy curves into a 3-ohm load are shown, in Fig. 12. Data of this sort, obtained at intervals over a period of 1 year, show in general that aging increases the type of delay characterized by the exposed environment, and that, accordingly, longer periods are required for energy to build up to a given level.

An experimental determination was made (Fig. 13) of the optimum load for an impulse cell acting over a 3-second interval. Predicting this result is impracticable in view of the uncertainty in voltage response.

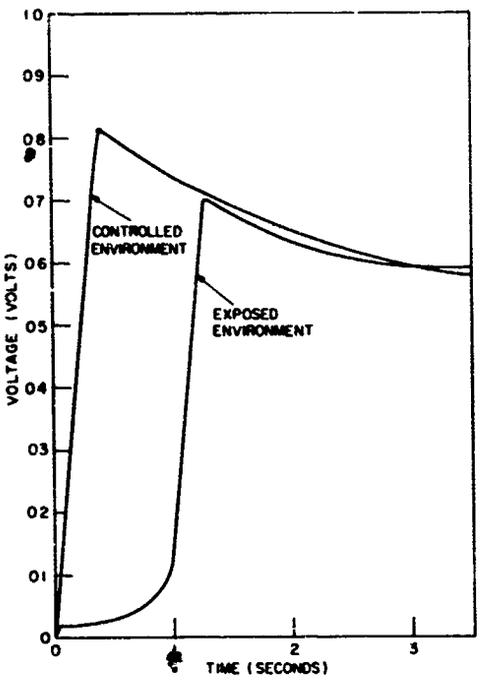


Fig. 11 - Typical impulse battery voltage response. The elapsed storage age is 6 weeks. The specimen size is 1 by 1 inch. The anode is Mg (AZ-31B), and the cathode is Ni and Pd plated. The cell load is 3 ohms, and the cell spacing is 0.03 inch.

BATTERY ELECTROCHEMISTRY AND ELECTRODE PERFORMANCE

Qualitative Electrochemical Model

An electrochemical model is instructive toward understanding the chemical stoichiometry, the site of the significant electrochemical reactions, and the identity of the charge carriers around the closed current path. This last feature couples the electrochemical model to the previously mentioned equivalent circuit, which is the more useful tool for actual design of a battery to a specific set of load conditions and environments.

Equations for a model useful in dealing with reactions extant in this type of battery may be postulated as

Anode	$Mg \rightarrow Mg^{++} + 2e^-$
Cathode	$2H_2O + 2e^- \rightarrow 2\,OH^- + H_2$
Net Reaction	$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$,

plus a local anodic reaction identical to that of the net reaction. Note that no indication is given for the role of sea salts as ionic charge carriers. These relations, however, imply that the electrolyte constituency remains constant for the large electrolyte source in which the sea-water battery is normally operated. From the electrolysis of water apparent in the model equations, however, it is obvious that electrolyte concentration would increase if battery operation were to take place in a relatively limited electrolyte supply.

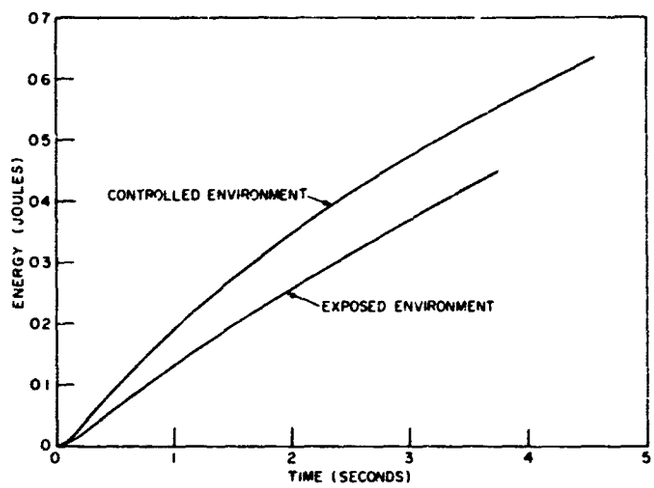


Fig. 12 - Energy curves for impulse batteries (same batteries as in Fig. 11)

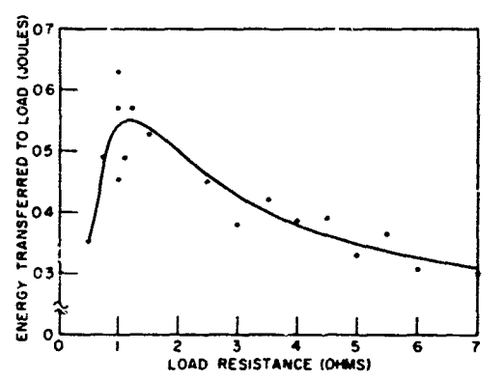


Fig. 13 - Energy transferred to the load over a 3-second interval vs load resistance. The cell characteristics are identical to those in Fig. 11.

For the battery or power-source engineer concerned with charge-carrier mechanisms, a diagrammatic representation may be related to the previous equations and is shown in Fig. 14. In this diagram the role of the Na^+ and Cl^- ions as the principal charge carriers is introduced. Other ions such as K^+ and Ca^{++} present to a lesser extent, share this electrolyte carrier current function.

The current continuity around the complete circuit is described by (a) the migration of Mg^{++} ions to a point where they join with 2 $(OH)^-$ or 2 Cl^-, both junctures comprising the current continuity condition in the general anode region of the electrolyte, (b) Cl^- migration toward the anode, (c) OH^- migration toward the anode due to Cl^- depletion and Na^+ attraction, (d) Na^+ motion toward the cathode with continuity junctions of Na^+ and OH^-,

and (3) electron motion in the external circuit from anode toward cathode. The diagram also indicates $Mg(OH)_2$ formation both from direct reaction of Mg^{++} with OH^-, particularly as a local anode reaction, and from reaction of intermediary products NaOH and $MgCl_2$.

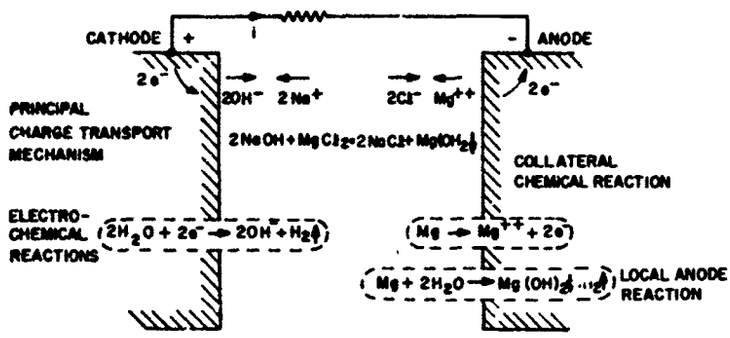


Fig. 14 - Inert-cathode/Mg-anode sea-water cell depicting the electrode reactions and the principal charge-carrying mechanism in the electrolyte

In view of the kinetics of the electrode reaction under load condition, no attempt is made to treat voltage conditions. Obviously this available potential from Mg ionization serves both to supply energy to the load and bring about the electrolysis at the cathode. The sense of cell incremental or component potentials are apparent from the current directions, the nature of the Mg/H_2O interface as a source, and the role of the load, electrolyte, polarization, and electrolysis as equivalent or actual resistive loads. The magnitudes are best evaluated by measurement, the voltage-current characteristics yielding sufficient information for power-source calculations.

Effect of Cathode-Surface Treatment and Texture

Since the cathode substrate is steel, its catalytic properties are enhanced by a Pd plating. But prior to this, Ni plate is first laid down, on top of which the Pd is plated. The results of these studies show that the role of the Ni plate is primarily one of rust inhibiting during prefuse storage or standby. This is brought out in Fig. 15, where a slight diminution in performance is observed in the presence of Ni from that of Pd alone. The effect of a Ni-only plating is also shown in Fig. 15 for comparative purposes.

The effective area enhancement of the cathode is made apparent also in Fig. 15, where perforated or expanded metal exhibits a gain over the plain sheet. The screen shows a further gain. A complete comparative quantitative behavior for cathodes with these types of texturing has not been fully explored. Figure 16 shows how mesh size affects screen performance, all other factors being constant. Although the figure shows continued performance gain with increase in mesh fineness, this performance gain does not continue indefinitely. On the one extreme, increasingly finer mesh would approach an embossed solid plate in surface equivalence, whereas on the other extreme, a coarse mesh would eventually approach a diminishing area condition. A finer mesh may result in some performance gain as indicated but introduces battery fabrication problems due to lack of rigidity. A larger self-supporting mesh may be worth some tradeoff in power performance. Coarser mesh may also contribute to better electrolyte circulation worthy of further power performance tradeoff.

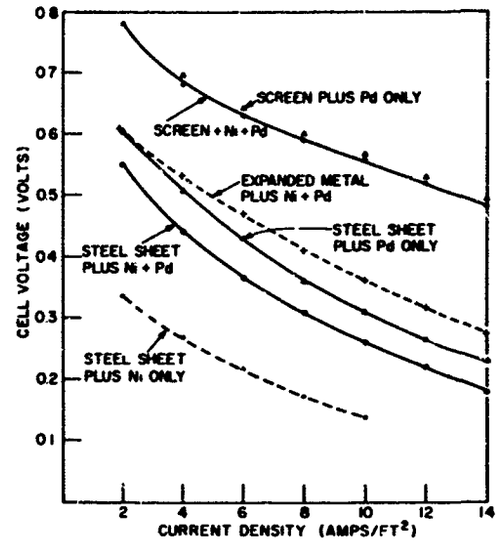


Fig. 15 - Effects of cathode-surface treatment and texture. Cell conditions and specimen sizes are identical to those of Fig. 1.

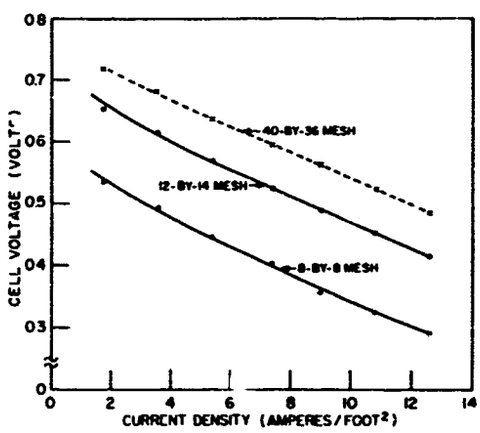


Fig. 16 - Representative effects of cathode-screen-mesh size. The anode is Mg (AZ-31B). The cell spacing is 1/8 inch, and the specimen cells are 2 by 4 inches.

A reduced performance per cell from that of the screen-cathode case will result from use of plates, say for applications requiring duplex (bipolar) electrodes in a series-battery configuration, or for cathodes plated on plastic substrates. Such tradeoff in performance may be warranted, however, in view of gains in construction economies. The 0.001 to 0.0035-inch-thick steel foil is cited for its economy in cost, weight, and space.

The voltage-current characteristics reported here represent a compromise between cost and performance. Further improvements in performance may be achieved by resorting to the more elaborate catalytic technology, such as has been developed for fuel-cell technology. In one instance reported recently, the gains in performance by use of high-quality platinized electrodes (5) in a sea-water electrolyte shows little advantage over that reported here for the plate-type electrode, remaining inferior to the screen-type electrode of Fig. 1. Furthermore, the insoluble reaction products intrinsic to the operation of this cell tend to adhere to the cathode and counteract the depolarizing effect of catalyzers no matter how effective they are, a property usually evaluated under idealized electrochemical conditions.

Fortunately, for low but usable current densities at least, this gradually increasing coating or scaling of the cathode, in particular, remains pervious to the electrolyte carriers

and allows Mg-anode wearout to a degree characteristic of such Mg erosion. Unfortunately, this perviousness does not persist for higher current densities, a fact which requires a tradeoff between life and current density or power.

Effect of Variation in Magnesium-Anode Alloy

The behavior of Mg alloy as an anode material has been rather well documented (8-11), although the erosion mechanism(s) accompanying the predominant oxidation are of a hypothetical status (8). For purposes at hand, however, three alloy types have demonstrated the ability to function as anodes as well as can be realistically expected. This sea-water cell may be construed as a simple discharge cell, the Mg anode serving as the source of energy to supply the load and effect electrolysis-producing OH^- ions at the cathode. In addition, the Mg ionization energy must also supply polarization and electrolyte resistance losses. Any enhancement of Mg-alloy activity is, then, absorbed largely in these internal losses. More important is the role of the Mg in reducing the intercellular clogging tendency characteristic of these cells (11).

Experience has shown that Mg with Al% and Zn% alloys, AZ-31B and AZ-61, and a special proprietary alloy from the General Electric Company have met the needs which these batteries could reasonably be expected to satisfy. For higher rate, short-term operation the AZ-61 and General Electric alloys exhibit higher output per unit cell size or lessen the clogging tendency due to a greater sloughing of the alloy surface, which carries off the steadily depositing reaction products. This process continually renews the anode surface, which, it is felt here, is the principal reason for the continued higher output over the shorter intervals of operation, appropriate for cells using these anodes. Pure Mg demonstrates performance equal to or better than the AZ-31 and AZ-61 alloys for short periods of operation but accumulates a film of the reaction products too quickly for practical purposes.

At the relatively high discharge rate of 22 amperes/square foot, the following relative voltage performance was demonstrated among the three alloys in identical screen-cathode systems: AZ-31B-100%, AZ-61-117%, and General Electric alloy-127%. A more general comparison, however, is shown in Fig. 17.

Anode Corrosion Rate

Previous considerations with respect to battery performance dealt primarily with power, i.e., voltage and current quantities. Since the battery energy is stored entirely in the Mg, meeting total energy requirements reduces to providing an adequate volume of Mg. In addition, it must be possible to feed this Mg "fuel" into the electrochemical reaction process. A battery of parallel-electrode construction permits the Mg energy to be released to the reaction process simply and reliably over one or both of its sides. The wearout rate for such Mg plates varies between 1/6 to 1/3 mil per hour for a current density of 1 ampere/square foot. The former rate is typical of short-operating-period cells for the AZ-31 alloy. However, for long operating durations, the Mg corrodes unevenly (Fig. 5) and the 1/3-mil-per-hour rate is typical for the AZ-31 alloy.

In most instances, practical considerations of battery construction result in an excess of Mg volume for reasons of retaining structural integrity over battery operating life or perhaps cost where the added expense of a limited quantity of thin Mg is not warranted even for very short operating life.

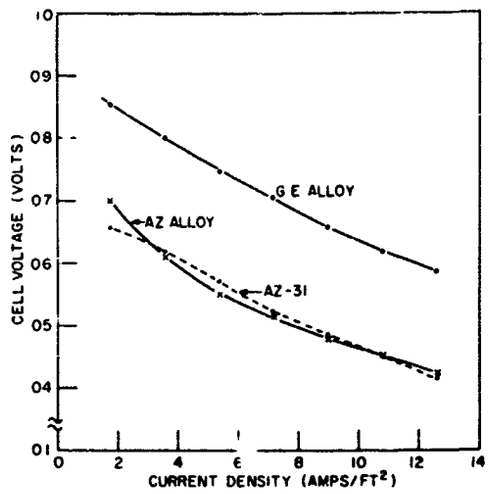


Fig. 17 - Effect of various anode alloys. The cells are of identical size, spacing, and cathode construction.

Other Effects

The clogging problem has been partially resolved for long-term operation with regard to the need to limit current density and to provide adequate interelectrode spacing with plate-type cathodes. But the results may require readjustment for applicability to the higher rate screen-type cathode cells, a fact which poses a problem for further study.

So-called end effects refer to differences between currents expected from predictions on a per unit area basis and those actually experienced due to the influence of geometrical configuration. Two illustrations point up these effects. One illustration is that of scaling up the current of a small cell to a square-foot basis, resulting in an apparent current density larger than that actually experienced for a cell with a square-foot dimension. This result is due to the fact that the small cell generally has so-called edge or even backside current components, in greater proportion to its area than would a cell with an area of a square foot. This effect is present in the model voltage-current characteristics presented here, which accounts in part for predictions higher than achieved in some instances. The other illustration is that of placing many smaller cells in parallel in achieving a net large area in order to achieve compactness. Considerable end effect arises in such an instance, commonly to the extent of yielding higher output than predicted.

Storageability and Reuse

The property of long storage capability is due to the absence of electrolyte and the inherent properties of the cathode and anode. The Ni provides the principal passivation ingredient for the cathode; the $Mg(OH)_2$ and oxides insulate the Mg alloy (8).

As a general rule, the inert-cathode/Mg-anode cell is best used in a one-shot primary battery. But due to the great convenience of its abundant and harmless electrolyte, reuse presents great temptations. No general conditions are available at this time to circumscribe reuse criteria. Batteries have been operated in the laboratory intermittently over a year's period for periods up to 2 to 3 hours, being rinsed and dried in the interim, without noticeable change in performance. Over a 3-day period batteries were activated hourly on an 8 to 10 hour per day basis, being dried between use, each time performing satisfactorily. A more sensitive ready-to-use storage capability exists for the impulse type of battery, calling for the greater attention given its storageability in a previous section.

CONSTRUCTIONAL ASPECTS

By securing voltage-current information for any particular cathode and anode material and texture, viz., plate, screen alloy, and spacing, batteries may be designed for an almost limitless variety of battery configurations and sizes (Fig. 18). A stacked plate or electrode construction with 1/16-inch to 1/8-inch spacing has proven the most utilitarian and rugged for short and intermediate term applications, including that for series batteries. It is important to allow ample porting for gas evolution and escape of insoluble reaction products. By operating the battery with the electrodes in a vertical position, this is normally accomplished by leaving at least the top and bottom open, thus permitting gas evolution from the top and escape of insoluble reaction products from the bottom. The latter are principally those that slough off from the anode. An appreciable amount of the finely divided $Mg(OH)_2$ precipitate is also carried away through the top of the battery by electrolyte circulation, some of which is promoted by the gas evolution.

Enclosing the sides serves to provide alignment and clamping for the electrode array. For the series battery, it serves additionally to provide cell isolation, further isolation being furnished by barrier extensions at the top and bottom. Batteries with relatively large-plate areas require electrode separators appropriate to the electrode extent and rigidity. These may serve the dual role of connectors and electrode positioning fasteners.

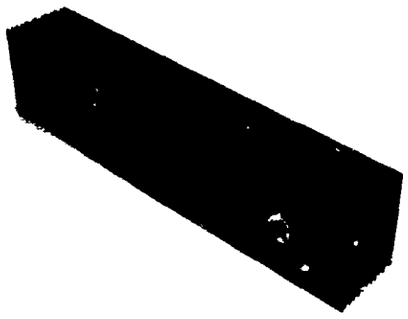
For the smaller batteries, spot-welded Ni-wire connections to both cathode and anode have proven satisfactory. The relatively high resistivity of the Ni calls for short lengths, additional lengths of these leads being made up of ordinary tinned copper.

For the type of cells considered here, the cathode may be either steel plate, expanded metal, or screen mesh, first plated with Ni and then with Pd. Pd alloys may be equally effective in their catalytic performance (12) but were not adapted here in the interests of economy. Commercial Ni sheet and screen did not serve well to augment the catalytic action of the Pd when subject to normal cleaning for Pd plating. In fact, as cited previously, the best results for procedures followed here in cell preparation occurred for Pd plating over the bare steel substrate. The cathode rusting and corrosion upon exposed storage was considered too great a price to pay for the small gain in performance over that of Ni plus Pd plating on a steel substrate. The Ni plating, based on experience with these cells, has therefore served as an effective and cheap rust preventive rather than a catalytic agent as it is, for example, in modern fuel-cell technology. In the case of fuel cells, however, the preparation of the Ni for low overvoltage electrodes is vastly more complex, the Raney (13) and Justi (14) electrodes being two examples. Cost estimates based on measured deposits are Pd-20¢/square foot and Ni-0.034¢/square foot.

SUMMARY

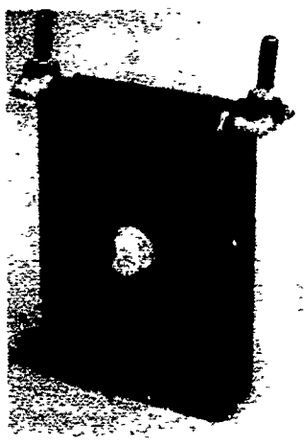
From the characteristics defined above for the inert-cathode/Mg-anode cell, it is possible to design batteries serving a wide variety of applications in the low power range. The considerable economy and nearly indestructible and timeless storage capability augur favorably for applications requiring large numbers of expendable-type units. However, the attributes of a specific tailor-made battery, and the ease and speed with which it may be constructed, also suit this class of battery to many highly specific applications, particularly where cost and environmental factors work to the disadvantage of existing modular battery packs.

For investigators stimulated to further pursuit of problems extant on this inert-cathode system, the extension of operating life at relatively high power offers the most fruitful challenge now apparent. Control and disposition of reaction products is at issue here. Uniformity of anode wear must also be achieved.

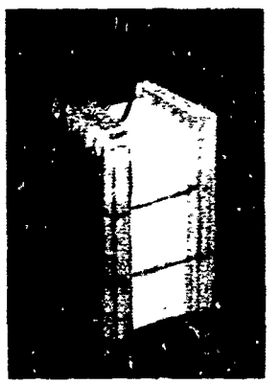


(a) Parallel cell

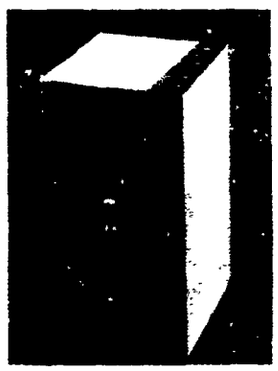
(b) Parallel cell



(c) Parallel cell



(d) Series battery



(e) Series battery

Fig. 18 - Typical batteries

Although experience is required to design within 10 to 20% of actual performance, the most significant consideration for practical operation involves temperature and salinity conditions. Providing adequate output at the lowest expected temperature and salinity sometimes results in excessive voltage at higher temperature and salinity conditions. This is readily controllable, however, by the converter which usually operates in conjunction with the battery. The lowered system efficiency resulting from this control is not serious for short-term operation, in view of the abundance of low-cost energy afforded by the Mg but should be carefully considered for long-term operation.

The screen cathode not only improves power output capability but also dramatically extends cell operating life by over a factor of five. The reasons for this lifetime protraction remain unknown. The flakelike electrode deposits characteristic of the plate cathode no longer arise on a screen cathode. Instead, a bulk deposit surrounds the screen wires and remains pervious to ion flow. Spectrographic analysis reveals only $Mg(OH)_2$ for both instances.

Limited sea trials disclosed that laboratory tests are representative of ocean operation, particularly for periods short of those where marine growth and fouling are encountered.

The great drawback of low cell voltage and operation of cells in a common electrolyte becomes apparent in series configurations. The greater profusion of reaction products (H_2 and $Mg(OH)_2$) than experienced in conventional batteries prevents practicable cell isolation beyond that offering net battery voltages of 2 to 6 volts.

The impulse capabilities of these cells, which arose out of serendipity, offer great potential for low-unit-cost squib-firing batteries with long ready-to-deploy shelf life.

Why should the inert-cathode/Mg-anode system take on any more significance today than previously? Its intrinsic low cell voltage was known then as now, but today there are the increasing cost and strategic criticality of Ag, and the solid-state converter, to recognize. The former speaks for itself. The latter has become a highly developed device capable of efficiency of 70 to 90%, adaptation to integrated circuitry, high reliability, and potential for low cost. This last attribute is significant. Without this, the economy gains of the battery would be offset by converter cost. There appears at present to be no roadblocks to the achievement of overall electric sources, i.e., battery plus converter, at power levels below 1 kilowatt, which will have superior combined economy and reliability for ocean-based application.

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13. ABSTRACT

The inert-cathode/Mg-anode sea-water battery has demonstrated the capability to furnish power, generally in conjunction with a dc-dc converter, for a variety of marine underwater devices. A battery of this sort may be tailored to application and its performance predicted to within 10 to 20% of actual. The focal point for the design process is the cell-voltage/current-density characteristic, which varies with electrode materials and conditions of use. The variations of this characteristic and its dependence on conditions of use are essentially circumscribed in this discussion.

Shelf life is long, upward from several years, on the basis of experience and materials. This shelf life presumes storage without the electrolyte and refrigeration. One exception exists in the case of the impulse cell where exposed storage periods in the order of 1 year lessens the magnitude and rate of cell response upon activation and the energy supplied over a given interval. Such loss may generally be compensated by initially allowing a greater margin of power. Operating life is adversely affected by accumulations of reaction products and varies with electrode spacing and current density. More than 60 days of continuous operation have been achieved at the reduced current density of about 1 ampere per square foot.

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14 KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Sea-water batteries						
Cell voltage						
Current density						
Mg anode						
Steel cathode						
Ni-Pd plating						
Underwater ASW						
Surveillance systems						
Power sources						

Series-battery terminal voltages of about 1.5 volts are conveniently achieved in the interests of compactness and converter efficiency. Higher voltages in series systems are achieved with greater cell isolation.

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