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Design characteristics of an aluminium–air battery with consumable wedge anodes

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An attempt was made to optimize a mechanically rechargeable bipolar-cell battery, exemplified by an aluminium–air battery with self-perpetuating wedge anodes. The optimization involved current density of battery operation and some design parameters such as the anode thickness and the cell dimensions. It was shown that these parameters depend on the energy-to-power ratio selected by the user. The saline electrolyte aluminium–air battery was found to be essentially a low power-density/high energy-density power source. Energy densities of up to over 1500 W h kg^{-1} are achievable for low power needs, indicating very long operations between recharging. It was also shown that aluminium should render significantly cheaper electric energy than any of the high-energy density metals.

Nomenclature

d	anode plate thickness (cm)
d_p	thickness of end-plates (cm)
d	thickness of cell walls (cm) (see Fig. 1)
E	energy density (W h kg^{-1})
E_B	total energy contained in the battery (kW h)
F	the Faraday constant 26.8 A h mol^{-1}
g_c	weight of the air cathode per unit anode area (g cm^{-2})
g_e	excess electrolyte per unit electrode area (g cm^{-2})
g_h	weight of the hardware per unit anode area (g cm^{-2})
g_m	weight of metal per unit electrode area (g cm^{-2})
g'_m	excess of unconsumable metal per unit electrode area (g cm^{-2})
g_o	sum of all the weights except that of consumable metal (g cm^{-2})
g_{ox}	weight of oxygen consumed with g_m (g cm^{-2})
G	total weight of battery (g)
G_m	total amount of reserve metal per cell and per cm width (kg cm^{-1})
G'_m	total weight of the wedges (kg)
G_r	total weight of the reserve anode container except the metal (kg)
ΔG	free energy of oxidation of the metal (kW h mol^{-1})
h_a	height of the wedge (cm)
h_r	reserve anode height (cm)
j	current density (mA cm^{-2})
J	total current drawn from the battery (mA)
n	number of electrolyte replacements between anode replacement
n_c	number of cells in a battery
M	atomic weight of the metal (kg mol^{-1})
P	power density (W kg^{-1})
Q_e	cost of metal in the cost of unit energy produced (\$ kW^{-1} h^{-1})
Q_e^0	theoretical figure of merit of a metal (\$ kW^{-1} h^{-1})
Q_m	cost of metal per unit weight (\$ kg^{-1})
S_a	total anode surface area (cm^2)
U	cell voltage without ohmic drop (V)
V	cell voltage (V)
x	width of battery (cm)
z	number of electrons exchanged per atom of metal dissolved
δ	interelectrode spacing (cm)
Δ	spacing between cover and top of a new reserve anode (cm)
η_f	material efficiency
η_v	voltage efficiency
κ_e	conductivity of electrolyte (ohm^{-1} cm^{-1})
ρ_e	electrolyte density (g cm^{-3})
ρ_m	density of metal (g cm^{-3})
ρ_p	density of end-plates (g cm^{-3})
ρ_w	density of cell-walls (g cm^{-3})

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1. Introduction

The choice and optimization of a battery is subject to a number of intangibles as well as to variables which can be submitted to quantitative treatment. Thus, a choice between an electrically rechargeable battery and one in which the energy is supplied by replacing active materials (mechanically rechargeable battery) depends on the availability (and economic feasibility) of the electric energy distribution network, transformers, chargers, etc. The choice between an alkaline and a neutral salt battery of the same type (e.g. mechanically rechargeable), depends on a delicate balance between the need for power density and voltage on the one side and potential hazards to the consumer, environmental acceptability, technical complexity, etc. on the other. The intangibles make room for, and divide the market between, different types of batteries. The market boundaries and capacities then are a problem for marketing investigations.

Quantitative optimization concerns a given type of battery to which the intangible factors have given a preference within a certain field of application. In this communication it was assumed that for a given market the mechanically rechargeable (consumable anode) metal–air battery [1, 2] (MRB) of given power, energy capacity and voltage is indicated. Hence, the choice of anode material, electrolyte, battery shape and construction is to be considered. The wedge-shape cell described elsewhere [1], is selected here, since it provides operation at a constant interelectrode spacing.

2. The choice of anode material

In the field of MRB two anode materials have emerged as technically and economically feasible: zinc [3] and aluminium [1]. Other metals, e.g. magnesium, calcium, lithium alloyed with aluminium and sodium, should also be considered.

The fact is that application of zinc in alkaline solution is a reality with aluminium following it closely, but this is at the development stage. Nevertheless, a rational comparison of all the potential candidates should be made. This must be based on a techno-economic criterion. The latter rests on the assumption that all other components of a battery are the same and that the cost of the anode material represents a significant portion of the overall cost of energy. Figures of merit for different materials can be evaluated as follows:

Let the free energy of oxidation of the metal for forming an oxide dissolved or dispersed in an aqueous solution be ΔG, the voltage and the current efficiency be η_v and η_f, respectively, and the cost of the metal per unit weight be Q_m, then the cost of metal consumption in relation to the cost of unit energy produced should be

$$Q_e = Q_m M \left[\left(\frac{\Delta G}{zF} \eta_v \right) zF \eta_f \right]^{-1} = Q_m M (\Delta G \eta_v \eta_f)^{-1} \qquad (1)$$

where M is the atomic weight of the metal. This can be taken as the figure of merit for the given metal as the anode material.

The theoretical figure of merit, Q_e^0, is that for which η_v and η_f are assumed to be unity. This is given for a number of metals in Table 1, and as the limit of possible achievement, it can serve as a stimulus for initiating research. However, in some of the most attractive cases, such as aluminium, magnesium and lithium, it is so far from present reality that it is hardly worth considering. Instead, on the basis of accumulated experience one can set targets which are within foreseeable achievement. This results in the last column of Table 1.

One can see that aluminium is by far the best proposition for electrical energy production in a neutral saline metal–air battery, being almost four times cheaper than zinc.

Table 1. Cost of metal consumption per kWh of energy produced

Metal	$M \times 10^{-3}$ *(kg mol⁻¹)*	Q_m *($ kg⁻¹)*	ΔG *(kWh mol⁻¹)*	Q_e^0 *($ kW⁻¹ h⁻¹)*	η_v	Q_e *($ kW⁻¹ h⁻¹)*
Li	6.94	44.15*	0.125	2.45	0.65	3.77
Na	23.0	2.052†	0.116	0.407	0.58	0.70
Mg	24.32	2.958‡	0.158	0.455	0.51	0.89
Al	26.97	1.66§	0.219	0.204	0.44	0.46
Zn	65.38	1.324¶	0.0884	0.979	0.60	1.63

*99.9% (Source: *Metal Bull.* (1984) 6852).
†(Source: *Chem. Marketing Reporter*, 2.1.1984).
‡(Source: 'Metalstatistik 1972–82', Metallges. Ag., Frankfurt a. M., quotation for *1982*).
§99.7% (Source: *Metal Bull.* (1983) 6850).
¶99.95% (Source: *Metal Bull.* (1983) 6850).

3. The problem of power density and energy density

The power density and the energy density (calculated on the energy obtainable between replacements of anodes) in MRB are functions of the amount of active material, but with opposing trends.

The power density of a given source operating at a selected (otpimized) current density, j (mA cm^{-2}), with a cell voltage V (V) is given by

$$P = \frac{Vj}{g}\,(\mathrm{W\,kg^{-1}}) \tag{2}$$

where g is the total weight of the battery G (g), divided by the total anode surface area S_a (cm^2).

In considering the latter one should note particular characteristics of the MRB of the metal–air type:

(a) the weight of the battery increases during operation as a consequence of the consumption of oxygen from the air and its inclusion in the weight of the reaction product (hydroxide, hydrated oxide, oxide) which stays in the battery. Hence, besides the weight of the metal g_m (g cm^{-2}) needed for energy production between replacement of anode, one must also take into account this weight of absorbed oxygen g_{ox}

(b) the electrolyte is taken up (chemically or physically) by the reaction product during the operation of the battery. Hence, the amount of the electrolyte between the electrodes $\delta\rho_e$ (g cm^{-2}) (δ is the interelectrode spacing and ρ_e the electrolyte density) is usually insufficient to accommodate all the reaction product formed between rechargings. An excess of electrolyte g_e (g cm^{-2}) is therefore needed

(c) the battery must be refilled with aluminium plates before all the metal is used.

Fig. 1 gives schematically the cross-section of a wedge-shape cell with a consumable wedge anode. It consists of three parts: the active part is in the middle (cell), with two air electrodes on the two sides encasing the wedge which is reproduced automatically during anodic dissolution as the aluminium plate slides downwards. Thus, a constant interelectrode spacing is maintained. The top part houses excess aluminium (reserve) serving as the feed to the cell. The bottom part is the electrolyte sump which houses excess electrolyte and serves as a collector for the precipitating alumina. If a constant current density is to be maintained at a given current drain, with the type of cell shown in Fig. 1, the battery is to be recharged when the anode sinks to the point E. Hence, it is, in fact, the entire wedge that must be always in the battery, representing an unavoidable excess of unconsumable metal g_m' (g cm^{-2}).

Hence, in view of these considerations

$$g = g_m + g_c + \delta\rho_e + g_{ox} + g_e + g_m' + g_h = g_m + g_0 \tag{3}$$

where g_c and g_h are weights per unit anode area (g cm^{-2}) of the air cathode and all the battery hardware, respectively, and g_0 sums up all the weights except that of the consumable metal.

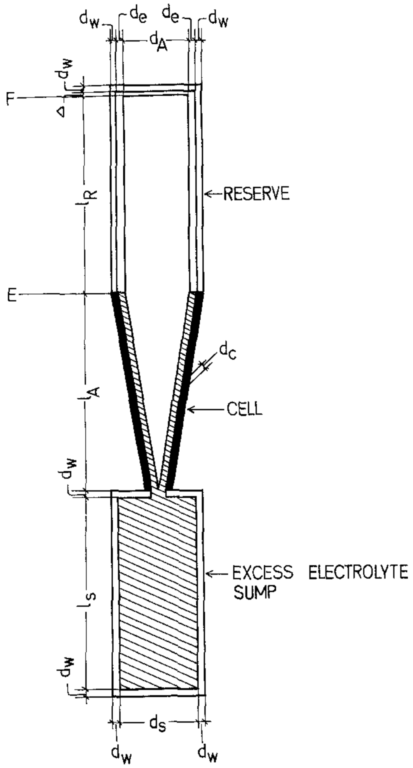

Fig. 1. Schematic representation of a mechanically rechargeable cell with self-perpetuating wedge anode.

Introducing Equation 3 into Equation 2 one obtains

$$P = \frac{Vj}{g_0 + g_m} \ (\mathrm{W\,kg^{-1}}) \tag{4}$$

The energy density is given by

$$E = \frac{(g_m/M)zFV\eta_f}{g_0 + g_m} \ (\mathrm{W\,h\,kg^{-1}}) \tag{5}$$

where z is the number of electrons delivered per atom of metal, F is the Faraday constant (26.8 A h mol^{-1}) and M is the atomic weight of the metal (kg mol^{-1}).

It is seen that with increasing g_m the power density decreases from a maximum level given by $g_m \to 0$, towards a hyperbolic dependence at $g_m \gg g_0$. At the same time the energy density increases at first linearly (for $g_m \ll g_0$) to tend to a maximum level independent of a further increase in g_m.

An example of the two trends is worked out for an aluminium–air battery with cells of a design given in Fig. 1. The result is given in Fig. 2, where the amount of consumable metal is expressed also in terms of the anode plate thickness.

One should note at this point that in the MRB there is a possibility of not placing into the battery all the electrolyte needed to completely consume the metal. In that case, however, it is necessary to replace the electrolyte more frequently than to recharge the metal. The battery capacity can then be referred to discharge between replacement of the anodes ('the aluminium range') or to that between the replacement of the electrolyte ('the electrolyte range'). If n electrolyte replacements are made between anode replacements, the power density is somewhat increased, since $(g_{ox} + g_c)$ in Equation 3 is divided by n.

The energy density calculated on the electrolyte range, however, is significantly decreased since, in spite of some decrease in g_0, the denominator in Equation 5 must be divided by n.

Considering Fig. 2 it becomes obvious that the choice of the amount of metal (or anode plate thick-

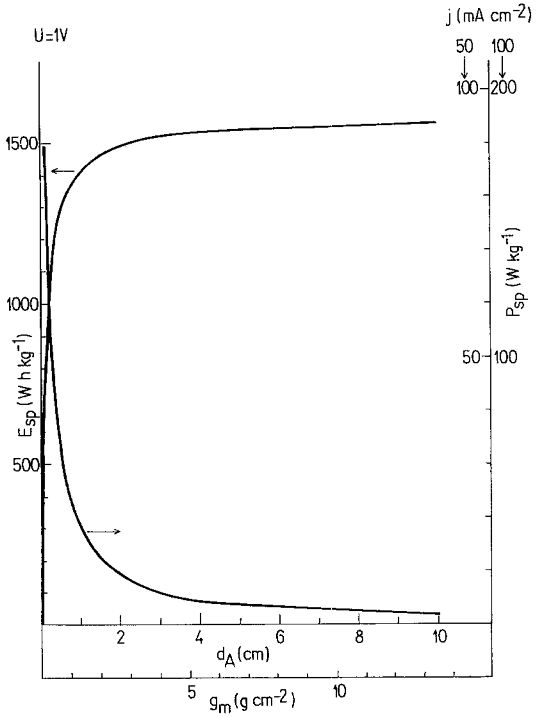

Fig. 2. Calculated energy density and power density for the battery based on cells shown in Fig. 1 (dimensions $l_A = l_R = l_S = 10$ cm, $d_w = d_e = d_c = 0.1$ cm, $\Delta = 0$, $d_S = d_A$) as functions of the amount of aluminium per cm^2 of the anode surface area (g_m) and anode plate thickness (d_A). Assumed cell voltage 1 V at operating current densities alternatively of 50 and 100 mA cm^{-2}.

ness) to be replaced in the battery will depend on the user's requirements for power and energy. Dividing Equation 4 by Equation 5 and solving for g_m one obtains

$$g_m = \frac{Mj}{zF\eta_f}\frac{E}{P} \tag{6}$$

One should note that the energy density-to-power density ratio is the same as that for the total energy and total power required by the user. It is interesting that g_m required for a given $E:P$ ratio is independent of the cell voltage or any other parameter of the battery contained in g_0 and increases with the current density used.

For example, for a 100 kW h per 10 kW aluminium–air battery Equation 6 gives (for $\eta_f = 1$) $g_m = 3.33j$ (g cm^{-2}) and for a reasonable range of j (10–100 mA cm^{-2}) g_m changes in the range between 0.033 and 0.33 g cm^{-2}. The required surface area of all the anodes in the battery is hidden behind this result. Obviously, for the same power a current density of 10 mA cm^{-2} implies electrodes which are ten times larger than those at 100 mA cm^{-2}, which must affect the weight of the hardware as well.

The interdependence between E and P can be obtained by eliminating g_m from Equations 4 and 5. One obtains a normalized power as

$$\frac{P}{(j/g_0)} = V - \frac{M}{zF\eta_f}E \tag{7}$$

which is a linear function, the slope of which depends on the two fundamental properties of the anode material M and z. The power that can be extracted for a certain E value depends on cell voltage at the given j and is larger the larger the ratio between j and the weight of all other components except the active metal charged per unit electrode surface area.

4. Optimization of operational variables

The operational variables are the current density (j) and temperature (T). Temperature functions are not known, except for the conductivity, but the experience gathered so far indicates that the electrode performance is not very sensitive to temperature. In any case, as the data are accumulating it will be interesting to perform all the subsequent assessments as functions of the operating temperature as well.

The operational variables can be optimized on the basis of the known behaviour of the system and independent of cell and battery design, assuming that the anode and the cathode are parallel to each other.

To perform the optimization it is necessary to know the voltage–current density relationship, $U(j)$, of the aluminium–air couple, the dependence of η_f on j, as well as the conductivity, κ_e, of the electrolyte. The former can be deduced using polarization curves for both the aluminium [4] and the air electrode [5] appearing in the literature. The dependence of the material efficiency, η_f, on current density depends very much on the source of the anode material and should be determined basically by the negative difference effect for the given material. (In the case of for example, high purity aluminium, it amounts to a current density-independent value of about 0.86.) The value of the conductivity can be found in tables.

The optimization is based on the maximum power density obtainable per unit electrode area, for this determines the minimum size of the battery for a given application and for a selected energy density within limits given by Equation 7.

The power density function per unit surface area can be obtained by elaborating on V and g in Equation 2. Thus,

$$V(j) = U(j) - \frac{\delta}{\kappa_e} j \times 10^{-3} \tag{8}$$

while g is taken from Equation 3.

Introducing Equation 8 into Equation 5 and solving it for g_m one obtains

$$g_m = \frac{E g_0}{(zF/M)V(j)\eta_f(j) - E} = \frac{E(g_c + \delta\rho_e + g_{ox} + g_e + g_h)}{(zF/M)[U(j) - (10^{-3}\,\delta/\kappa_e)j]\eta_f(j) - E} \tag{9}$$

Introducing Equations 8 and 9 into Equation 4 one obtains

$$P = \frac{\{[U(j) - (10^{-3}\,\delta/\kappa_e)j]\eta_f(j) - (M/zF)E\}j}{(g_c + \rho_e\delta + g_{ox} + g_e + g_h)\eta_f(j)} \tag{10}$$

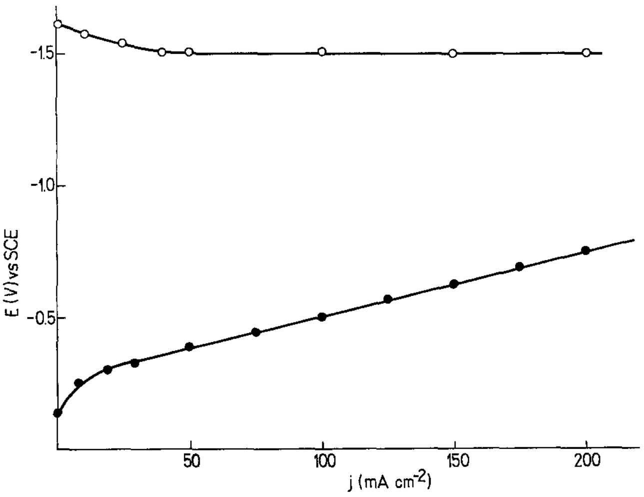

Fig. 3. Anodic and cathodic polarization curves for an aluminium–gallium (0.2%) alloy and for an air electrode, respectively, as found in the literature [4, 5].

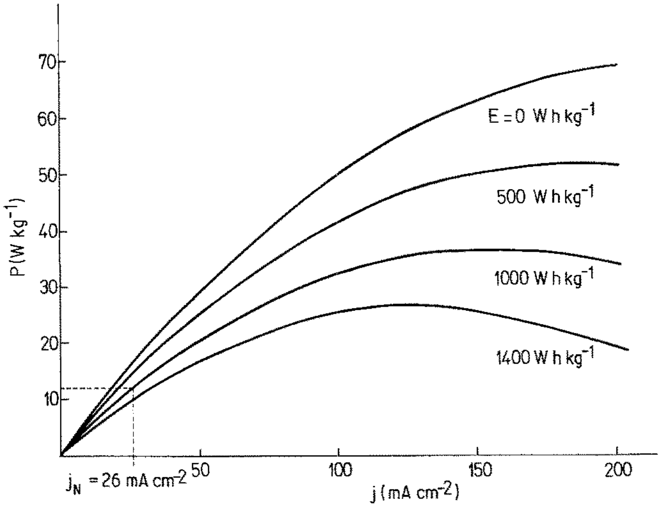

Fig. 4. Calculated power densities as functions of current density for different energy densities of an ALAIR battery of the type shown in Fig. 1. Nominal current density j_N determined for $E = 1000\,\mathrm{W\,h\,kg^{-1}}$ as 1/3 of the current density for maximum power.

A typical example is worked out for an aluminium–air battery working at ambient temperature for which the anode and cathode potential–current density relationships were taken from the literature [4, 5] to establish $U(j)$, as shown in Fig. 3, and κ_e was taken to be 0.2 mho for a saline electrolyte. With $\delta = 0.1$ cm, $\rho_e = 1\,\mathrm{g\,cm^{-3}}$, $g_c = 0.1\,\mathrm{g\,cm^{-2}}$, $(g_{ox} + g_e + g_h)$ assessed to be about $2\,\mathrm{g\,cm^{-2}}$ and $\eta_f(j) = 0.86$ (independent of j), one could calculate the $(P–j)$ relationship shown in Fig. 4.

Since a battery has to have an overload capacity to stand an unusual load without damage, it is a common practice to take the current density at a third of the peak power as the reasonable nominal current density of operation.

5. Battery design and optimization of design parameters

Characteristic of MRB is the anode consumption during operation tending to increase the interelectrode spacing. This problem could be dealt with in several ways. The most recent development is that of a bipolar cell with self-perpetuating semi-wedge anode (SPW) [6] shown schematically in Fig. 5.

The anode sinks as it is consumed and the constant δ is maintained automatically. Contacts between adjacent cells are maintained through a conducting wall with sharp protrusions made of a hard material scratching the anode and providing numerous point contacts. In this way the transfer of current between cells meets negligible resistance. This arrangement with flat-plate anodes, offers the most economic use of space.

Several considerations affect proportioning of the battery. The desired voltage determines the minimum length of the battery, composed by cell stacking. Since standard voltages are desirable (6 and 12 V for the low voltage range and 110 to 220 for network connected installations), it is the cell thickness and the number of cells in the battery, n_c, which determines the total length of the battery.

From the graph in Fig. 2 one can see that, for example, a selected energy density of $1000\,\mathrm{W\,h\,kg^{-1}}$ for a battery proportioned as in Fig. 1, would imply a cell thickness of 0.5 cm.

The width, x, is limited by the problems of air circulation. Hence, it is not possible to assess the optimum width at this stage without additional experimentation with cell models. The total height of the battery depends on three factors: (a) the need for total current; (b) the ratio between g_m and g_m' and (c) the amount of the excess electrolyte g_e.

The height of the semi-wedge anode is given by

$$h_a = \frac{J}{xj} \times 10^3 \tag{11}$$

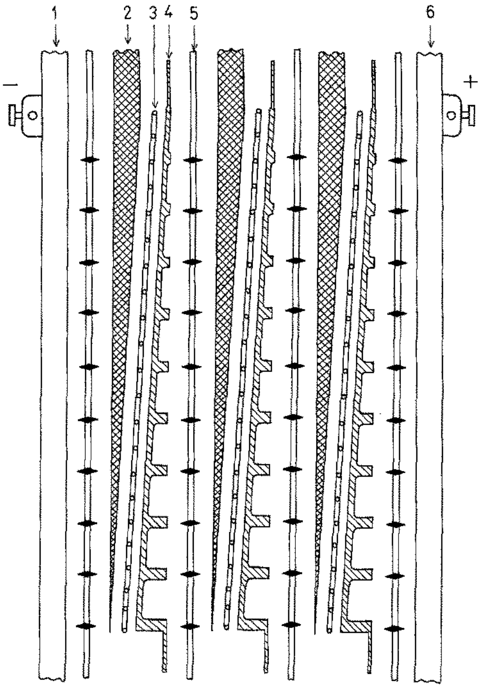

Fig. 5. Schematic representation of a bipolar aluminium-air battery with semi-edge anodes. 1, 6 – end-plates; 2 – aluminium anode; 3 – spacer; 4 – air-electrode; 5 – dividing wall.

where J and j are, respectively, the total current to be drawn from the battery under nominal conditions, and the nominal current density.

The height of the reserve metal compartment depends on the total energy to be contained in the battery, E_B, since this determines the total amount of reserve metal, G_m, per cell and per centimetre width

$$\frac{G_m}{xn_c} = \frac{ME_B}{zFV(j)\eta_f(j)n_cx} \times 10^3 \tag{12}$$

with n_c being the number of cells in the battery and x the width.

Within this amount the reserve anode height, h_r, and thickness, d, can be varied, for,

$$h_r d\rho_m = \frac{G_m}{xn_c} \times 10^3 \tag{13}$$

The increase in height results in an increase in the weight of the reserve anode compartment and the two end-plates, while the increase in anode thickness results in an increase in the weight of the metal in the wedge, g'_m. Hence, the two quantities can be optimized.

The total weight of the upper part of the battery containing reserve anodes, G_r, as a part of the total weight, G_0, comprising all except the metal to be consumed, G_m, is given by

$$G_r = [2\rho_p d_p + n_c d_w(x + 2d + 6\Delta + 6d_w)\rho_w]h_r \times 10^{-3} \tag{14}$$

where ρ_p and d_p are the density and the thickness of the end-plates, respectively, ρ_w is the density of cell walls and the meaning of the other symbols is shown in Fig. 1.

The total weight of the wedges is

$$G'_m = \frac{n_c\rho_m h_a}{2} d \times 10^{-3} \tag{15}$$

To optimize the contribution of these two items to G_0, one should first solve Equation 13 for h_r,

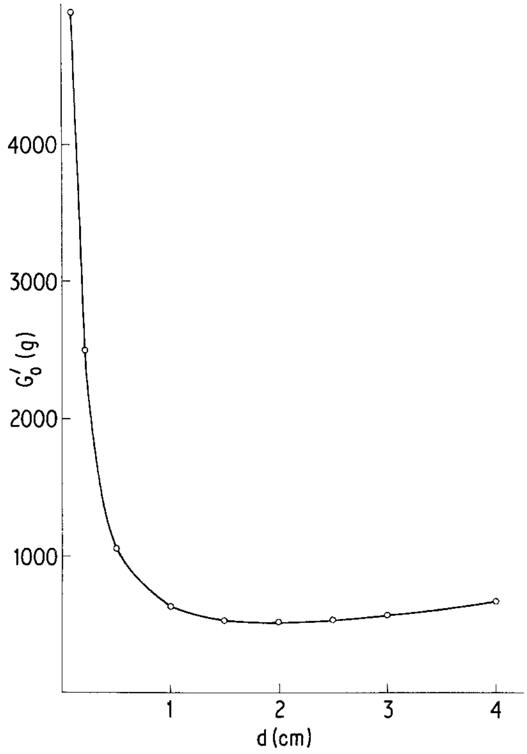

Fig. 6. Change in weight of a battery with changing reserve anode plate thickness (for details of calculation see Equation 11 and parameters cited in the subsequent paragraph).

replace this in Equation 14, and then sum up Equations 14 and 15. Thus,

$$G_0' = G_r + G_m' = [2\rho_p d_p + n_c \rho_w d_w(x + 6\Delta + 6d_w)] \frac{G_m}{\rho_m x n_c} \frac{1}{d} + \frac{n_c \rho_m h_a}{2} d \times 10^{-3} \qquad (16)$$

This function is shown in Fig. 6 for the following typical values of parameters: $\rho_p = 2.7\ \mathrm{g\,cm^{-3}}$; $d_p = 1$ cm; $n_c = 10$; $\rho_w = 1\ \mathrm{g\,cm^{-3}}$; $d_w = 0.1$ cm; $x = 20$ cm; $\Delta = 0.1$ cm; $\rho_m = 2.7\ \mathrm{g\,cm^{-3}}$; $h_a = 10$ cm and $G_m = 10$.

The optimum for the anode plate thickness is seen to be around 2 cm, implying a reserve anode height (cf. Equation 13) of about 9 cm.

In general the optimum is found from

$$\left(\frac{\partial G_0'}{\partial d}\right) = \frac{n_c \rho_m h_a}{2} \times 10^{-3} - \frac{[2\rho_p d_p + n_c \rho_w d_w(x + 6\Delta + 6d_w)]G_m}{x \rho_m n_c} \frac{1}{d^2} = 0 \qquad (17)$$

that is,

$$d = \left\{\frac{2[2\rho_p d_p + n_c \rho_w d_w(x + 6\Delta + 6d_w)]G_m}{\rho_m^2 h_a n_c^2 \times 10^{-3}}\right\}^{1/2} \qquad (18)$$

which, for the above set of parameters, renders $d = 1.92$ cm and $h_r = 9.63$ cm.

With this anode plate thickness the total length of the ten cell battery, including the end-plates should be about 14 cm.

Assuming the excess electrolyte sump to be also 10 cm high, the dimensions of the battery should be about 14 x 20 x 30 cm, with a total energy output of 36 kW h and a total nominal power of about 50 W, providing a 720 h operation between additions of new reserve anode plates.

One should note that the optimum battery dimensions are rather sensitive to the total energy required since the latter determines the total amount of metal G_m. Thus, for ten times less energy the optimum plate thickness is 0.6 cm, h_r is 3 cm. With the same assumption that the excess electrolyte sump is of the same dimensions as the reserve anode compartment the battery dimensions are now 10 x 20 x 16 cm.

In conclusion, one may state that, for each specific application, the evaluation of the optimum battery dimensions and especially the decision on the load of the metal and the electrolyte, can be made a matter of a rational assessment based on the quantitative relationships derived above.

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