

## REFUELABLE BATTERIES

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In the non-fossil fuel society, it is proposed (1) that electricity will be generated by nuclear power stations which will be situated in underpopulated areas for environmental and safety reasons. Since gas transmission is cheaper than electricity transmission and since the demand for power is not constant, it is suggested (1) that hydrogen will be produced at these nuclear power stations and transported via pipeline to the consumer where it will be used for heating, cooking etc. and for the local production of electricity via fuel cells.

In this hydrogen fueled society, electrochemical power sources will replace the hydrocarbon fueled equipment which is presently used for many mobile and portable applications. The high power applications (e. g., automobiles, trucks) may be served by fuel cells. However fuel cells are only practical in situations where 1) the total energy requirement of the system is high and the weight of hydrogen is a large percentage of the total system weight and 2) the required power is sufficiently high to justify the weight of the ancillary controls. They are not suitable either for low power applications since the fuel cell has a minimum weight which is determined by the weight of the ancillary equipment, or for portable applications since the hydrogen tanks cannot be readily carried.

Thus there are many medium power (1/2 KW - 5 KW) devices (e. g., outboard motors for boats, lawnmowers, motor bikes, camping equipment) which use hydrocarbon fueled engines at present but which will require low cost, high energy and power density batteries in the non-fossil fuel society.

Lead acid, nickel/cadmium, nickel/iron secondary batteries will probably continue to provide rechargeable energy sources for applications where their low energy density and cost/KW are relatively unimportant. However for reasonable cycle life (e. g., > 200) all of these storage batteries have energy densities less than 20 watt-hours/pound and this is a major deterrent to their use in many lightweight portable devices or traction vehicles where cost, weight and operating range are important.

The limitations of the present storage batteries have stimulated research in high energy density systems such as 1) secondary zinc/air cells, 2) organic electrolyte cells and 3) molten salt cells. However these internally rechargeable batteries (i. e., charged by applying a direct current to the electrodes while they are contained in the battery) suffer from the following limitations:

- 1) They have limited cycle life at high depths of discharge,
- 2) For long cycle life (hence low depths of discharge) storage batteries have significantly lower energy densities than primary batteries,
- 3) Charging at low rates (i. e., overnight) limits the type and extent of use of the device,
- 4) The charging efficiency at high rates of charge is low.

Thus a new battery system is required for the medium power applications in the hydrogen fueled society and refuelable batteries are one possibility.

In this paper we will review the present technology of refuelable metal/air batteries and discuss the future research required on these systems. We have not set out to make a clear cut case for these batteries over other electrochemical power sources (such as fuel cells and molten salt batteries) but rather our aim is to point out the advantages and disadvantages of the metal/air system in the hydrogen

fueled society. In particular we will describe novel methods of recharging the anodes which will be applicable due to the availability of hydrogen.

### 1. Refuelable Batteries

In principle a refuelable battery is one in which the discharged plates can be easily replaced. In practice it is simpler to replace only the anode and mechanically rechargeable metal/air batteries are the only refuelable batteries which have been developed.

In metal/air batteries, the oxidant (air) reacts with an electropositive metal to form a metal oxide (or hydroxide) and electrical energy. Mechanically rechargeable metal/air cells are refueled by withdrawing only the discharged anodes and replacing them with new ones. The advantages of these batteries are:

- 1) The discharge efficiency of the anodes is 80% or greater and this allows high energy densities to be obtained,
- 2) They are capable of giving high power densities,
- 3) They can be refueled (recharged) rapidly since the anodes can be readily removed and replaced,
- 4) The charging efficiency is high since the spent anodes may be recharged externally at a low rate,
- 5) There is flexibility in anode regeneration (Section 6),
- 6) The oxygen cathode is used only during discharge and then it is capable of many cycles.

Thus it can be seen that refuelable batteries could be recharged rapidly and still use off-peak power for anode regeneration so that extra fuel cell capacity would not be required for battery charging (low capital cost).

By reviewing the present technology of mechanically rechargeable metal/air batteries, we can define some of the limitations of such batteries and then describe the improvements that are required and the likelihood of their being achieved.

We will restrict this review to the following cells: zinc/air, aluminum/air, magnesium/air, iron/air and cadmium/air. These systems have been included since: 1) they have high theoretical energy densities and 2) several studies have been made with them so that their problems are well-defined. Other cells with high theoretical energy densities (e. g., lithium/air and sodium amalgam/air) have not been included since their state of the art is not far advanced (2).

Lead/air batteries have not been included (although the anode is well-developed and carbonate formation in the acid electrolyte is not a problem) since: 1) they have a low theoretical energy density (183 Wh/lb), 2) the cost per watt-hour of lead is high (.77¢/KWh), 3) only expensive, noble metal cathode catalysts are stable in the acid electrolyte, 4) the cathode polarization is significantly higher in acid than in alkaline electrolyte (3) and 5) Pt dissolves in the electrolyte and is transported to the anode (i. e., lowers its  $H_2$  overvoltage), thus decreasing the anode shelf life and preventing efficient recharge.

### 2. Design of Refuelable Batteries

Mechanically rechargeable zinc/air batteries have been used by the military for communications equipment (2, 4-6) and similar designs have been used for Al/air (2, 7), Mg/air (8-11), Fe/air (12) and Cd/air (2, 13) cells.

The basic cell consists of two cathodes (0.200 - 0.250 inches apart) connected in parallel and separated by a porous zinc anode inserted between them.

With this design it is simple to remove a discharged anode from the bicell and replace with a new one. Figure 1 shows the arrangement of anode and cathode, Figure 2 shows the bicell design and Figures 3 and 4 show 2 battery designs.

The present zinc anodes are made from zinc powder which is impregnated with dry potassium hydroxide and then pressed to the required dimensions. The electrodes are wrapped in a separator (a few thousandths of an inch thick) and stored in aluminum/mylar envelopes to retard water pick-up and zinc oxidation.

The air electrodes (Figure 1) must be held flat and parallel to the negative plate to minimize  $iR$  losses in the cell and to prevent electrode shorting but the lightweight air cathodes are not sufficiently rigid to be dimensionally stable. Thus non-compressible, porous spacers are placed in the air chambers between bicells and then subjecting the whole cell stack to an external pressure which is applied by a screw adjustment (Figure 4). Pressure is released to allow refueling (replacement of zinc plates) and reapplied before the next discharge. Obviously this requires that the tolerances on the dimensions of the zinc electrodes must be within a few thousandths of an inch.

Air flow is generally achieved by natural convection and the space between the bicells is therefore a critical design factor. The air spacing is a compromise between the need to provide sufficient air for high discharge rates and the need to minimize the volume of the battery. Forced air convection is used to increase the battery power density. However this results in a lower energy density due to the extra weight of the fan and to the parasitic current drawn from the battery and in faster carbonation of the electrolyte (Section 5).

### 3. Technology of Metal/Air Cells

Table 1 gives values of the E.M.F.'s ( $E$ ), the theoretical energy densities, the thermoneutral voltages ( $E_T$ ) (2) and the anode cost per theoretical KWh of metal/oxygen cells. The theoretical energy densities were calculated from the electrochemical equivalent of the anode and the cell E.M.F.

Table 1 lists the thermoneutral voltages of the metal/oxygen couples. This parameter is defined as  $-\Delta H/RT$ , where  $\Delta H$  is the enthalpy of the cell reaction. It is an abstract quantity and it represents an unachievable voltage at which no heat would be generated by the cell.

The thermoneutral voltage permits simple calculations of heat generation in metal/air cells. For example, the ratio of the heat generation to electrical power is given by  $(E_T - E_C)/E_C$ , where  $E_C$  is the cell operating voltage, and this ratio is useful in comparing the heat generation of the metal/air cells.

Figure 5 shows the polarization curves for metal/air cells. Clearly these polarization curves will depend on many parameters (e.g., anode and cathode manufacturing technique, anode porosity, cathode catalyst etc.) which will vary from manufacturer to manufacturer. However the curves in Figure 5 do give an indication of the expected initial performance of the metal/air cells.

The polarization curves for Al/ and Mg/air cells were obtained with a chloride electrolyte (NaCl or KCl) while those for the other metal/air batteries were obtained with an alkaline electrolyte (31% KOH). The curve for Zn/air cells

TABLE 1

## Energy Densities of Selected Metal/Oxygen Couples

Reaction	E. M. F. (1) (V)	Energy Density (Wh/lb)	Thermoneutral Voltage (V)(3)	Cost(4) (\$/theoretical KWh)
$2Al + 3/2 O_2 \rightarrow Al_2O_3$	2.71	3665	2.93	0.07
$2Mg + O_2 \rightarrow 2MgO$	3.09	3090	3.11	0.12
$2Fe + 3/2 O_2 \rightarrow Fe_2O_3$	1.28	836(5)	1.42	0.10
$2Zn + O_2 \rightarrow 2ZnO$	1.62	603	1.80	0.25
$2Cd + O_2 \rightarrow 2CdO$	1.20	260	1.35	9.14

1. For air ( $P_{O_2} = 0.21 \text{ atm.}$ ), 11mV should be subtracted from these potentials
2. Calculated from the electrochemical equivalents of the metals and the cell E. M. F. (3)
3. Thermoneutral Voltage =  $-\Delta H/nF$
4. Based on the cost of metal ingot
5. This value is for the oxidation of the metal to the 3 valent state. The energy density for the oxidation of Fe to the 2 valent state is 557 Wh/lb.

is the best literature value (14) and it was presumably obtained with thin electrodes since the cell voltage depends on the anode thickness (15). For example, the voltage at  $100\text{A}/\text{ft}^2$  for a zinc/air battery with a 0.200 inch thick anode was 0.1V less than the value given in Figure 5 (4). The polarization curve for the Cd/air cell was obtained (2) with a 0.030 inch thick commercial Cd anode and those for the Al/ and Mg/air cells were obtained with alloy sheet anodes. No polarization curves have been reported for alkaline electrolyte Fe/air cells in the literature and the data given in Figure 1 was calculated on the assumption that the Fe/air cells voltage would be 0.4V less than that of Zn/air cells. This assumption agrees with the cell voltages calculated from half cell data of iron electrodes (16) and of air cathodes (Figure 6).

Table 2 gives values of the ratio of the heat generation to electrical power at a discharge rate of  $40\text{mA}/\text{cm}^2$ . This data was calculated using the value of the operating voltage at  $40\text{mA}/\text{cm}^2$  from Figure 1 and the cell thermoneutral voltage (Table 1). Dissipation of this heat is important even in zinc/air batteries (Table 2).

TABLE 2

Heat Generation by Metal/Air Cells

Couple	$\left( \frac{\text{Heat Generation}}{\text{Electrical Power}} \right)^{(1)}$ at $40\text{mA}/\text{cm}^2$
Al/air	1.15
Mg/air	1.78
Fe/air	0.61
Zn/air	0.46
Cd/air	0.55

(1) Calculated from the thermoneutral voltages (Table 1) and the operating voltages at  $40\text{mA}/\text{cm}^2$  (Figure 5).

#### a) Zinc/Air

Zinc anodes offer a compromise between Al and Mg anodes on one hand which have high theoretical energy density but poor use-life and polarization characteristics, and Cd anodes which have low theoretical energy density but good shelf-life and polarization characteristics. The anodic behaviour of zinc is determined by its relatively high hydrogen overvoltage and the solubility of zinc oxide in alkaline solution. The former means that Zn has a relatively long shelf-life and this can be further increased by amalgamation while the high solubility of zinc oxide prevents zinc passivation and allows high discharge rates to be obtained.

The anode thickness and porosity are determined by the required energy and power densities and typical values of these parameters are 0.05" - 0.250" and 75% - 85% respectively. The energy density of the cell is increased by increasing the cell capacity per unit area of cell (i. e., increase anode thickness and decrease anode porosity). However high power densities are only obtained by increasing the electrode porosity but this results in a lower weight of zinc in the electrode and hence in a lower energy density. Thus there is a trade-off between energy and power density.

A major limitation of the present zinc/air batteries is the heat genera-

tion at high rates of discharge. From the value of the thermoneutral voltage of this cell (Table 1) it can be seen that a zinc/air cell delivering electrical power at 0.9V must dissipate an equivalent amount of energy as heat. This is undesirable since it results in an increase in cell temperature which consequently: 1) increases the rate of zinc anode self-discharge and 2) causes water loss from the cells by evaporation.

It is difficult to compare values of energy density and power density from the literature since these two parameters are dependent on operating temperature, duty cycle of the battery and the cathode catalyst. Energy densities of 80 Wh/lb with power densities of 45 W/lb have been reported (5) for a 1/3 KW battery. A larger system (1 KW), which is closer to the system required in the hydrogen fueled society, demonstrated a maximum power-density of 26 W/lb at an energy density of 30 Wh/lb (14). The author (14) projected that further improvements might be possible up to limits of 80 W/lb and 80 Wh/lb but these goals have not been achieved at present. Neither of these batteries used forced air convection and therefore cannot be used to project power and energy densities for larger (5 KW) batteries.

The 1/3 KW battery mentioned above is used for military communications equipment. The cost of the batteries and of the replacement anodes is \$400/KWh and \$40/KWh, respectively. Thus with 100 discharge cycles, the operating cost is \$44/KWh. This is too expensive for non-military applications and it is necessary to decrease both the anode manufacturing cost and the cathode catalyst cost.

In summary the problems which limit the use of zinc/air batteries at present are:

- 1) The use-life of the Zn anode is limited and it is preferable to use these cells continuously rather than in intermittent operation,
- 2) The lower discharge efficiency of thick Zn anodes at high rates of discharge,
- 3) The heat generation at high discharge rates,
- 4) Since the oxidized state is soluble, the zinc oxide in the discharged anodes slumps to the bottom of the current collector and thus the shape of the electrode must be reformed during anode regeneration,
- 5) The cost and stability of the cathode catalyst.

#### b) Aluminum/Air

The high cell E.M.F., the high theoretical energy density, its low cost per watt-hour and the ease of manufacture of anodes makes aluminum an attractive anode for metal/air cells. However the aluminum/air cell has two major problems: 1) the discharge of aluminum anodes is irreversible and 2) the self-discharge of aluminum anodes is very rapid.

Aluminum electrodes dissolve rapidly on open circuit in alkaline solution with the evolution of hydrogen and consequently Al/air cells generally use either a neutral (KCl) or acidic ( $AlCl_3$ ) electrolyte (2). However even in this electrolyte, pure aluminum dissolves rapidly on open circuit and polarizes excessively. More reversible behaviour is exhibited by aluminum/tin alloys. Optimum performance (2) was obtained with the aluminum/tin alloy A6 (Olin Mathieson Chemical Corp.) and Figure 5 (2) shows the polarization curve of an Al/air cell with this alloy in a 2.5 MKCl solution.

As a consequence of the high self-discharge rate of Al alloy anodes and of the cell irreversibility, a major limitation of Al/air cells is the heat generation and Table 2 shows that for cells operating at the same power, Al/air cells generate approximately three times more heat than zinc/air cells. This heat generation results in a high rate of water loss, it creates hazardous and runaway conditions

and it severely decreases the anode shelf-life. It may be alleviated by using a large electrolyte reservoir or by forced air convection, but neither approach permits high energy density designs.

The advantages of Al/air cells are that the anodes can be made from sheets of the metal alloy which are simple and cheap to manufacture and they use a cheap, CO<sub>2</sub> rejecting, safe electrolyte which can be easily handled by the consumer.

No work has been reported on operable, mechanically rechargeable battery systems. Single cell data in alkaline electrolyte (7), have been used to project an energy density of 200 Wh/lb and a power density of 76 W/lb. However these values were calculated on the basis of the weight of the reactants only and the electrolyte and Al were separated while the cell was on open circuit. It is vital that the system includes adequate provision for cooling, since the experimental design data is based on cell voltages of 0.9 - 1.25 volts which indicates heat generation at 2 to 3 times the rate of power generation. Thus the total battery weight will markedly decrease the values of energy and power density and the energy and power density data quoted above (7) is considerably greater than would be obtained in an operable system.

#### c) Magnesium/Air

Magnesium anodes exhibit the same disadvantages as aluminum anodes, i. e., irreversible polarization characteristics and high self-discharge rates. In addition, the discharge product of Mg anodes is a solid sludge which masks the bottom portion of the Mg anode and makes anode removal difficult (8, 9, 11).

In alkaline electrolyte magnesium anodes passivate and Mg/air cells utilize a sodium chloride solution (11). Even in this electrolyte pure magnesium anodes polarize excessively and this has resulted in the use of magnesium alloys which are often ternary alloys of magnesium, aluminum and zinc. Figure 5 shows the polarization curve for a Mg/air battery using the Mg alloy AZ61 (Olin Mathieson Chemical Corp.) in 18% NaCl solution (11). As with Al alloys, low Mg alloy polarization is associated with a high rate of self-discharge and the alloy AZ61 gave the optimum performance.

The product of Mg anode discharge in a Mg/air cell is magnesium hydroxide (or hydroxylchloride) (11). This product remains in the cell as a sludge and the volume of the cell must be sufficiently large to contain this product and to allow easy removal of the anode after discharge.

Heat generation due to anode self-discharge and cell irreversibility is an even greater problem with Mg/air cells than with Al/air cells (Table 2). Thus Mg/air requires a water reservoir and/or forced air convection to aid in cell cooling and it has been shown that these cells operate more efficiently at low temperatures (10).

A 23 cell Mg/air battery of similar design to that in Figure 3 has been reported (11). From data given in the paper (11) and assuming the battery weight (4) is the same as that of zinc/air batteries (Figure 3), the battery energy density was approximately 65 Wh/lb and the maximum power density was 50 W/lb. Water evaporation during battery operation was a major problem and water had to be added to the cell, otherwise the Mg was not consumed uniformly and the cell voltage decayed (11).

#### d) Iron/Air

Iron anodes have been used for over fifty years in Ni/Fe batteries. The

advantage of this material is its availability, abundance and basically low cost.

The theoretical energy density for iron/air cells (Table 1) was calculated assuming the oxidation of iron to the 3 valent state. However the anodic discharge of an iron electrode in alkaline electrolyte occurs at two discrete voltage levels. The first at  $-0.8V$  vs Hg/HgO corresponds to the conversion of iron to ferrous hydroxide while the second at  $-0.65V$  vs Hg. HgO corresponds to the conversion of iron to the three valent state (16, 17). The iron electrode is normally operated only to the first discharge voltage plateau (i. e., 2 valent state) and the theoretical energy density for the iron/air cell is then 557 Wh/lb.

Sintered iron electrodes have the ability to be deeply discharged and hence make lightweight, low cost iron electrodes a possibility. Low electrode cost, however, is dependent on developing an inexpensive means of increasing the  $H_2$  over-voltage of iron. This is presently achieved by refining the iron oxide powder to a high degree of purity before reducing it to powdered iron particles but this adds considerably to the electrode cost.

The advantages of iron/air cells compared with zinc/air cells are:

1. The lower cost of iron/KWh (Table 1),
2. Iron oxide is cation conductive and hence less prone to passivation,
3. There is no material slumping in the discharged anode since the oxidized state of the iron electrode is relatively insoluble.

No mechanically rechargeable Fe/air batteries have been reported although it has been claimed (12) that energy densities of 65 Wh/lb are achievable.

#### e) Cadmium/Air

The cadmium/air couple has the lowest theoretical energy density of the couples considered in this paper (Table 1) but thin (0.030 inches) cadmium electrodes are readily available and hence development costs for this cell should be relatively low. The cadmium/air cell (2) has a lower voltage at all current densities than the zinc/air cell (Figure 5) and the practical energy density is lower.

Refuelable cadmium/air batteries could be manufactured with today's technology but would probably not provide high enough energy or power densities to justify their high cost. Thus the lower cell voltage and the lower electrochemical equivalents probably (2) restrict the maximum achievable energy density for refuelable Cd/air cells to 20 Wh/lb.

The advantages of cadmium/air cells compared with the zinc/air systems are: 1) Cd anodes have good shelf-life, 2) Cd anodes have long cycle life and 3) the anode could be recharged without using d. c. power (18) which may be particularly advantageous in the hydrogen fueled society (Section 6).

#### f) Air Cathode

The cathode structure used in most metal/air systems (2) consists of a mixture of catalyst and Teflon (19) supported on a hydrophobic film with the current collected by an expanded metal mesh embedded in the catalyst/Teflon matrix. The Teflon aids in the formation of an air/electrolyte/catalyst three phase boundary which ensures that the maximum catalyst area is used efficiently in the electrochemical reaction. The hydrophobic film prevents electrolyte seepage from the cell and acts as the outer case of the bicell (Figure 2). The advantages of these electrodes are: 1) they are lightweight and the oxidant does not contribute to the cell weight, 2) they exhibit high limiting currents, 3) they exhibit a stable voltage

during discharge and 4) they exhibit a flat polarization curve which permits operation of the electrode over a wide current density without large voltage variations.

Figure 6 (2) shows the polarization curves for oxygen reduction on a Teflon bonded Pt electrode (Pt loading  $5\text{g}/\text{ft}^2$ ) in air saturated 31% KOH solution and in air saturated 2.5 M KCl solution. The cathode overvoltage (i. e.,  $E - E_C$ ) was plotted versus the current density (Figure 6), in order to compare the cathode polarization in alkaline and chloride electrolyte.

Comparison of the cathode polarization in alkaline electrolyte (Figure 6) with the Zn/, Fe/ and Cd/air cell polarization (Figure 5) indicates that the cathode polarization is the major fraction of total cell polarization up to  $100\text{A}/\text{ft}^2$ . Thus most of the heat is generated at the cathode in these cells and a decrease in the cathode polarization will markedly decrease the heat generated as well as increase the battery power density. A decrease in cathode polarization may be achieved either by increasing the catalyst activity (i. e., decrease the activation polarization) or by improving the electrode structure (i. e., decrease the concentration polarization).

Platinum has been used as the cathode catalyst in those applications (military) where high energy density is more vital than battery cost, but Pt cathodes are a major cost limitation of commercial Zn/, Fe/ and Cd/air batteries. For example, a zinc/air battery with a Pt catalyzed cathode ( $5\text{gms}/\text{ft}^2$  of Pt) gave  $100\text{ W}/\text{ft}^2$  ( $100\text{A}/\text{ft}^2$  @  $1.0\text{V}$  (4)) and the platinum cost was then approximately  $\$300/\text{KW}$ . Clearly such costs limit the commercial usefulness of present, refuelable zinc/air batteries and require far more than the 100 discharge cycles, which is obtainable at present (4), to be economically attractive.

Another reason why Pt cannot be considered as a practical catalyst is the gradual transfer of Pt from the diffusion electrode to the negative plate (20). This will clearly limit the number of cycles obtainable with the cathode and the presence of Pt on the anode will increase its rate of self-discharge and will lower the coulombic efficiency of anodes which are recharged electrochemically.

Carbon, on which a hydrogen peroxide decomposition catalyst was supported, has been used to decrease the cathode catalyst cost. For example, a zinc/air battery with a carbon catalyzed cathode containing  $1/4\text{ g}/\text{ft}^2$  of a noble metal gave (15)  $65\text{ W}/\text{ft}^2$  ( $65\text{A}/\text{ft}^2$  at  $1\text{V}$ ) and the catalyst cost was then approximately  $\$25/\text{KW}$ . However this lower weight of noble metal catalyst resulted in a greater cathode polarization, a low cell power density and greater heat generation.

The polarization of Pt catalyzed air cathodes is much greater in KCl solution than in KOH solution (Figure 6). This may be due both to the lower buffer capacity of KCl solution (concentration polarization) and to the influence of chloride ions on the catalytic activity of Pt (activation polarization). Comparison of the cathode polarization curves (Figure 6) with those for Al/ and Mg/air cells (Figure 5) indicate that in these cells approximately 50% of the heat evolution is due to cathode irreversibility.

There are no efficient catalysts for oxygen reduction in chloride electrolyte and the exchange current density for oxygen reduction on platinum was found to be a minimum at pH 7 (21). However polymeric cobalt phthalocyanine (22) has been shown to exhibit a lower polarization for oxygen reduction in neutral than in acid electrolyte and it may prove worthwhile to investigate the activity of these cathode catalysts in chloride electrolyte.

#### 4. Heat Generation and Dissipation

Heat is generated during the discharge of all metal/air cells. As a

result of the heat generation, the cell temperature must be controlled to minimize the anode self discharge rate and water evaporation rate. This is of particular importance in Al/ and Mg/air cells (Table 2) but cell temperature control is also very important with the other metal/air cells.

The provisions for heat dissipation are dependent on the discharge rate of the cell. Thus the higher the rate of discharge the greater the cell polarization and the greater the ratio of heat generation to electrical power.

Very little heat can be dissipated by conduction from the cells to the battery case since the lightweight current collectors are the only metal connection between cell and case. Therefore the major heat transfer path has to be to the air and hence the heat is dissipated by convective heating of the air and by water evaporation (2, 23). The relative contributions of these heat transfer modes depends on the cell temperature, water vapor pressure, air flow rate, inlet and outlet temperature, and the relative humidity of the air stream. The interdependence of these parameters is quite complex and the relationships have been derived for a 10 KWh zinc/air battery (2, 23).

Battery cooling is achieved either by the use of forced air convection or by using an excess of electrolyte. However both these solutions limit the cell energy density since they increase the battery weight and, in addition, the air circulation rates must be kept low to minimize the parasitic power drain and electrolyte carbonation.

## 5. Carbon Dioxide Removal

Adsorption of  $\text{CO}_2$  in the electrolyte occurs with all the alkaline electrolyte metal/air batteries. Carbonation of the electrolyte affects the metal/air cell performance by changing the electrolyte pH in the vicinity of the cathode, by precipitating carbonate in the cathode pores and by causing anode passivation.

With the present military zinc/air batteries the electrolyte is discarded after discharge of the anode, but this is an expensive maintenance procedure, it is hazardous and it presents disposal problems. It can only be tolerated for small batteries where the application permits the high operating cost and where weight and volume are at a premium. The carbonate concentration in larger alkaline electrolyte metal/air batteries must be controlled by scrubbing the  $\text{CO}_2$  from the atmosphere.

The removal of  $\text{CO}_2$  from the atmosphere has been studied for alkaline electrolyte fuel cells and has been reviewed in detail (24). Table 3 lists the expendable and regenerable carbon dioxide scrubbing systems which have been studied.

TABLE 3

Carbon Dioxide Removal Systems

Expendable Adsorbers	Regenerable Adsorbers
Soda Asbestos	Molecular Sieves
Lithium Hydroxide	Monoethanolamine
Soda Lime	Aqueous Caustic Alkali

### a) Expendable Adsorbers

Of the three expendable carbon dioxide adsorbers which have been studied

(Table 3), soda lime is generally preferred. Thus although LiOH has a 20% greater capacity for CO<sub>2</sub> adsorption, it is more expensive while soda asbestos tends to block if the air has a high humidity.

Soda lime was used as the air scrubber in a demonstration of an alkaline electrolyte fuel cell/lead acid battery power source for a small car (25). It was found that 20 lbs. of soda lime lasted for 500 miles of driving and from the data given it can be shown that this is equivalent to 1/4 lb of soda lime/KWh.

#### b) Regenerable Adsorbers

The required CO<sub>2</sub> levels can be achieved with molecular sieves but they can only be used in dry air and they require considerable power for regeneration.

The CO<sub>2</sub> concentration cannot be reduced below 30 ppm with a mono-ethanolamine scrubber and this is rather high for continuous use of the electrolyte. In addition there is a constant loss of ethanolamine due to vaporization and the material requires considerable heat for regeneration.

Aqueous caustic solutions have been investigated for scrubbing air for alkaline electrolyte fuel cells (24) and these solutions may be regenerated electrochemically. In the regeneration technique, hydrogen and oxygen are evolved at two electrodes and the regenerating cell is operated under mass transfer conditions so that the acid generated in the vicinity of the anode results in the evolution of carbon dioxide from the electrolyte. The major disadvantage of this system is the inefficiencies which result from the high overvoltage for oxygen evolution and from the concentration polarization required to reach a pH in the range 11-14. Polarization losses can be reduced if the anode and cathode are depolarized with H<sub>2</sub> and air respectively. Clearly this regenerative technique would mean a large parasitic power loss and it is necessary to have more details on the scrubbing efficiency of alkaline electrolyte and on the regeneration efficiency before it is known whether this system is competitive with soda-lime for small power levels.

### 6. Battery Refueling

Two processes are involved in the refueling of mechanically rechargeable metal/air batteries:

- a) Removing the discharged anodes and replacing them with new electrodes,
- b) Anode regeneration.

The battery system must be designed so that the former process can be carried out rapidly by unskilled personnel since speed of recharging is one of the major advantages of refuelable batteries. However the anode regeneration could be carried out slowly and use off-peak power (H<sub>2</sub>). Except for the reduction of cadmium oxide (Section 6(b)), reduction of the metal oxide is probably too complex to be carried out by the consumer and will have to be performed at service stations.

#### a) Anode Replacement

Practical experience has been gained recharging zinc/air batteries and a description of the recharging of these batteries serves to identify the problems in charging all metal/air batteries.

After discharge and removal from the bicell (Figure 2), the zinc electrode is little more than a conductor surrounded by a mass of zinc oxide particles in a separator bag which is wet with KOH solution. Because of the lack of cohesion between zinc oxide particles, anode shape change occurs during the battery discharge

(i. e., the zinc oxide slumps to the bottom of the plate) and the spent plate is no longer uniform. Thus these discharged anodes must be first pressed into approximate dimensions and then be restrained to these dimensions while they are cathodically reduced to zinc in alkaline electrolyte. They must then be removed from the reduction bath, washed free of KOH, dried and pressed to the exact cell dimension.

The disadvantages of using this type of zinc electrode are: 1) they have poor rigidity and adherence in the discharged state, 2) the regeneration process is complex and expensive, 3) porous zinc anodes impregnated with KOH are potentially hazardous and could not be handled safely by unskilled personnel, 4) re-generated zinc anodes of this form have a limited life before capacity degenerates to an unacceptable level because of particle size growth during each discharge/charge cycle.

These problems have led to the development of a zinc/air battery which utilizes a zinc powder (26). In this system (26), which is being developed as a power source for electric automobiles, the zinc powder fuel was stored as a suspension in water and distributed intermittently with electrolyte to the bicell. The bicell was similar to that in Figure 2 and the air cathodes were catalyzed by silver (loading 60 g/KW). After discharge the spent fuel and electrolyte was drawn from the battery and regenerated independently of the battery operation.

The major disadvantage of the cell was that a large volume of electrolyte was required for efficient discharge of the zinc powder (i. e., 4l of 10N KOH solution for 1 KWh), otherwise the zinc powder passivated. Thus a typical small electric car would need approximately 10 gallons of tank storage for a day's operation (10 KWh). On this basis, daily refueling would be desirable and would probably best be met by storing zinc powder and electrolyte in the car owner's garage. The authors did not indicate time needed for refueling. However this would probably require about 5 minutes since the battery has to be drained of electrolyte and ZnO and the tanks have to be replenished with a Zn/H<sub>2</sub>O slurry and with fresh electrolyte.

The battery had an energy density of 42 Wh/lb and a 10 hour operating capacity. Capital costs for the battery were quoted as \$100/KW, but this did not cover the fuel regeneration equipment and no data was provided to indicate this cost.

The work so far looks promising for the intermediate electric vehicle, but vast improvements would be needed for it to serve the hydrogen fueled society efficiently.

Magnesium/air and aluminum/air batteries offer greater flexibility for refueling since they use regular alloy sheet. The simplicity of this type of anode and the need for only minimal protection against bending during shipment and storage means that manufacturing costs would not be much higher than the cost of commercial alloy sheet. These anodes are also non-adherent after discharge but, since Al/ and Mg/air batteries use a chloride electrolyte, the spent anodes could be safely handled by the consumer. These discharged anodes could not be reprocessed by the consumer but they would be discarded and new ones would be purchased from a store. Thus the ease of refueling, reinforced by the fact that they use a cheap, CO<sub>2</sub> rejecting, safe electrolyte, provides an incentive for further research to develop a commercial Al/air or Mg/air battery.

Discharged cadmium and iron electrodes are rigid and adherent in the discharged state and thus many of the processes used in recharging Zn anodes would not have to be used in recharging Fe and Cd anodes. In addition the discharged anodes could be readily recharged in the hydrogen fueled society and hence the high initial electrode cost would be countered by the low regeneration cost.

## b) Metal Oxide Reduction

In the non-fossil fuel society, internally rechargeable batteries would be recharged by using the d. c. power from the fuel cell. However the electrochemical efficiency of the fuel cell is only 70% and the watt-hour efficiency of charging is at best (i. e., with slow charging rates) only 60-80%. Thus the volume of hydrogen used to recharge storage batteries would be two to three times greater than the theoretical value.

In this section we will describe methods of recharging discharged Fe, Zn and Cd anodes in the H<sub>2</sub> fueled society. Since the discharged anode is removed from the bicell and the metal oxide is reduced in a separate apparatus, hydrogen can be used directly for anode regeneration and this gives a particularly high charging efficiency. Discharged Al and Mg anodes cannot be reduced in aqueous electrolyte and it would be more convenient and economical to reclaim these metals by recycling.

There are three ways of recharging the discharged anode:

1. Reduction of the metal oxide by d. c. power using an inert counter electrode (oxygen evolution),
2. Reduction of the metal oxide by d. c. power using a hydrogen depolarized electrode as the counter electrode,
3. Thermal reduction of the metal oxide with hydrogen.

In Table 4 the operating costs (expressed as a volume of hydrogen) of each method are compared. The data in columns 1 and 2 (Table 4) were calculated assuming a fuel cell electrochemical efficiency of 70%.

In method 1 the discharged anode is cathodically reduced in an alkaline electrolyte bath using an inert counter electrode. Thus the applied voltage during charge is equal to the sum of the E. M. F. of the metal/oxygen couple and the total overvoltage for the electrode reactions. The data in Table 4 (column 2) was calculated by assuming that the total cell overvoltage during charge would be 0.6V.

The procedure in method 2 is similar to that in method 1 except that a hydrogen depolarized electrode is used as the counter electrode. Thus the applied voltage during charge is equal to the sum of the E. M. F. of the metal/hydrogen couple and the total overvoltage of the electrode reaction. The data in Table 4 (column 3) was calculated by assuming that the hydrogen overvoltage is 0.05V, and that the volume of H<sub>2</sub> required for the H<sub>2</sub> depolarized electrode is equal to the theoretical coulombic value.

Table 4 shows that it is significantly more expensive (larger volume of H<sub>2</sub>) to reduce the metal oxide by method 1 than by method 2. This is because the applied voltage during charge is less in the latter method since: 1) the E. M. F. of the metal/hydrogen cell is approximately 1.2V lower than that of the metal/oxygen cell and 2) the overpotential for H<sub>2</sub> oxidation is significantly less than that for oxygen evolution. For example, the Zn/ZnO electrode potential is only 0.4V more negative than that of hydrogen and thus, with a hydrogen depolarized counter electrode, the applied voltage for oxide reduction is only 0.45V, whereas the applied voltage is 2.2V with an inert counter electrode.

In the third method the metal oxide is reduced by heating in hydrogen. The data for this method (Table 4, column 4) was calculated by using the stoichiometric volume of hydrogen and no allowance was made for the hydrogen required to heat the oxide to the required temperature (i. e., these values are the theoretical volume of hydrogen required for anode regeneration).

Table 4 (column 5) also shows the minimum temperature required for the

TABLE 4

Energy Required (expressed as the volume of H<sub>2</sub>) to Recharge the Anodes

Anode	Volume of Hydrogen to Recharge Anode (SCF/KWh) (1)		Temperature of Oxide Reduction (°C)
	Electrical(2)	Thermal(3)	
	O <sub>2</sub> Evolved at Counter Electrode	Hydrogen Anode	
Fe <sup>(4)</sup>	21	12	500°C
Zn	22	13	> 1000°C
Cd	23	12	25°C

1. Volume of H<sub>2</sub> required to form 1 KWh of energy in the form of metal from the metal oxide based on the theoretical energy densities of the metal/oxygen couples.

2. Assuming the electrochemical efficiency of the fuel cell is 70%.

3. Calculated from the volume of H<sub>2</sub> required to reduce the oxide; No allowance is made for heating Zn and Fe to the required temperature.

4. Calculated for Fe (II).

thermal reduction of the metal oxide with hydrogen. These values were calculated using literature values of the free energy of formation of the oxides (27) and of the elements (28).

Direct reduction of ZnO occurs at too high a temperature (Table 4) for this method to be economical and thus zinc electrodes would be recharged by the cathodic reduction of the metal oxide utilizing a hydrogen depolarized anode.

Since the Fe/Fe(OH)<sub>2</sub> electrode is only slightly less noble than the H<sub>2</sub> electrode (0.05V), iron oxide can be reduced in a similar way but the external voltage would now only be 0.10V. However iron oxide may also be reduced by heating the oxide in a hydrogen atmosphere to a temperature of approximately 500°C (Table 4). This temperature was calculated by assuming that the anode discharge product was FeO since there was no information in the literature on the variation of the free energy of formation of Fe(OH)<sub>2</sub> with temperature. If little heat is needed, direct reduction of the discharged iron anode may be as economical as the electrochemical reduction and it is probably more convenient.

Reduction of CdO with hydrogen is possible at room temperature (Table 4) but the reaction is very slow. However cadmium oxide can be reduced by externally connecting the cadmium oxide to a hydrogen depolarized anode (18) and no external power need be applied for this process since the Cd/CdO electrode is more noble than the hydrogen electrode.

Clearly this technique for recharging Cd electrodes can also be carried out in the battery without removing the anodes from the bicells and this may possibly be carried out by the consumer. This would be done by sweeping air from the system with nitrogen and bleeding H<sub>2</sub> into the gas space behind the diffusion electrode. Each cell is then shorted out (positive to negative) until H<sub>2</sub> consumption ceases. The short-circuit is then broken and the N<sub>2</sub> - H<sub>2</sub> mixture replaced by N<sub>2</sub> again and then air. Thus this battery system needs only a H<sub>2</sub> supply and adequate gas-manifolding for recharging. The simplicity of the system however must be weighed against its initial cost and low energy density. Careful control of alkalinity is also necessary to avoid carbonate build-up and consequent short-cycle life of the cadmium electrode.

In this section we have only compared the operating costs (Table 4) of anode regeneration but the cost of the recharging equipment (capital cost) would partially determine the total battery recharging cost. At present there is no information on this cost but, if extra fuel cell capacity had to be added for battery recharging the capital cost would be markedly increased. However, in contrast to rapid charging of conventional storage batteries, refuelable batteries can be recharged rapidly and yet use off-peak power for anode regeneration.

## 7. Summary

This review has necessarily been restricted to mechanically rechargeable metal/air cells since these are the only refuelable batteries which have been developed. These refuelable batteries have many possible advantages over internally rechargeable systems but these advantages are counterbalanced by the problems with each metal/air cell.

Table 5 summarizes the cell energy densities and the present and possible future capabilities of the metal/air batteries. The first value of energy density (Table 5) was calculated from the electrochemical equivalents of the metals and the metal/air cell voltage at 40A/ft<sup>2</sup> (Figure 5). Comparison with the theoretical energy density values given in Table 1 indicate the influence of cell polarization on energy density. The second value of energy density given in Table 5 takes into account the total battery weight. These values were either obtained from the literature (Zn), or calcu-

TABLE 5

Capabilities of Metal/Air Batteries

Anode	Energy Density (Wh/lb)		Capabilities of Batteries	
	Wt. of Metal(1)	Battery(2)	Present	Future
Al	1894	No data	Low power density due to heat generation.	High energy and power density; cheap electrode manufacture.
Mg	1150	65	Low power density due to heat generation.	High energy and power density; cheap electrode manufacture.
Fe	607	65	Moderate power density.	Low operating cost; Moderate energy density.
Zn	457	80	Relatively high power density.	Low anode replacement and regeneration cost; Moderate energy density.
Cd	186	20	Low energy and power density.	Low operating cost.

1. Calculated from the electrochemical equivalents of the metals and the cell voltage at 40 A/ft<sup>2</sup> (Figure 5).

2. Values based on the total battery weight which have been reported in the literature or extrapolated from literature data.

lated from data given in the literature.

Clearly none of the existing metal/air cells meet the requirements of the hydrogen fueled society (Table 5) but neither do the present storage batteries (e. g., lead acid and nickel/cadmium). The improvements which must be made in order to improve the metal/air systems to the point where they will provide energy densities of 100 Wh/lb and power densities of 75-100 W/lb at acceptable costs/KW and /KWh are:

1. Cost of cathode catalyst,
2. Irreversibility of the cathode,
3. Heat generation by the battery,
4. Removal of discharged anodes from the bicell,
5. Adsorption of CO<sub>2</sub> by the electrolyte (alkaline electrolyte cells only).

In addition improvements must be made in each anode to achieve the goals listed in Table 5. Thus in order to make zinc/air batteries more viable the manufacturing cost and the recharging cost of zinc anodes must be decreased. To provide the basis for low cost, high energy density aluminum/ and magnesium/air batteries, Al and Mg alloys giving more reversible potentials and having a lower rate of self-discharge are required. The energy and power density of iron/air cells is limited by the electronegativity of iron but the intrinsically low cost of iron would allow low cost iron/air cells to be made providing the self discharge rate of non-purified iron can be decreased.

#### Acknowledgements

The authors thank Electric Storage Battery Inc. and Energy Conversion Ltd. for permission to publish the zinc/air battery photographs.

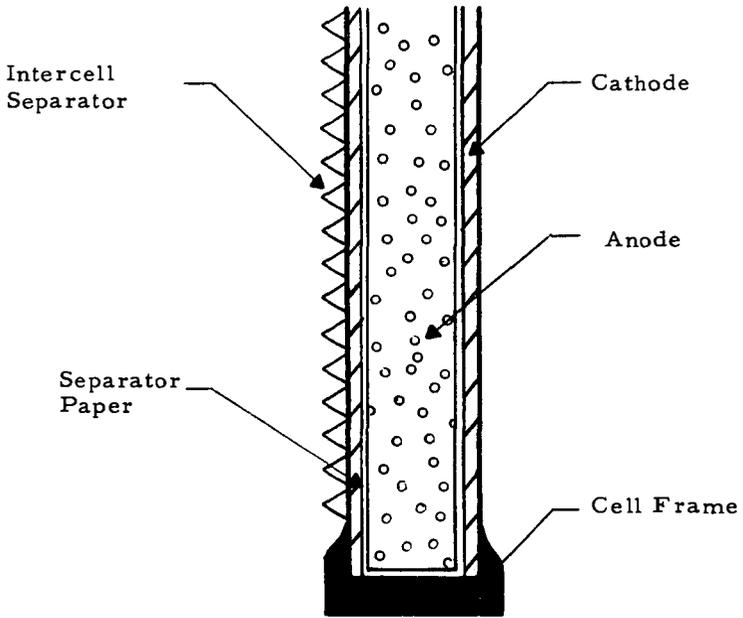


FIGURE 1 Diagram of Zinc/Air Bicell

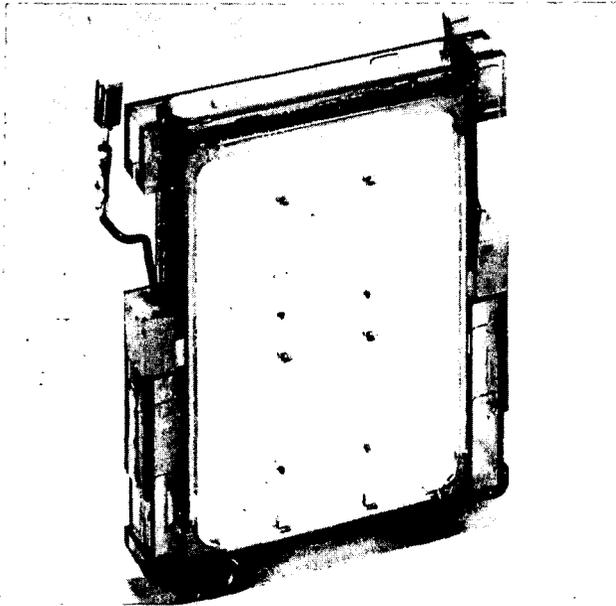


FIGURE 2 The Bicell



FIGURE 3 ESB INC. Zinc/Air Battery

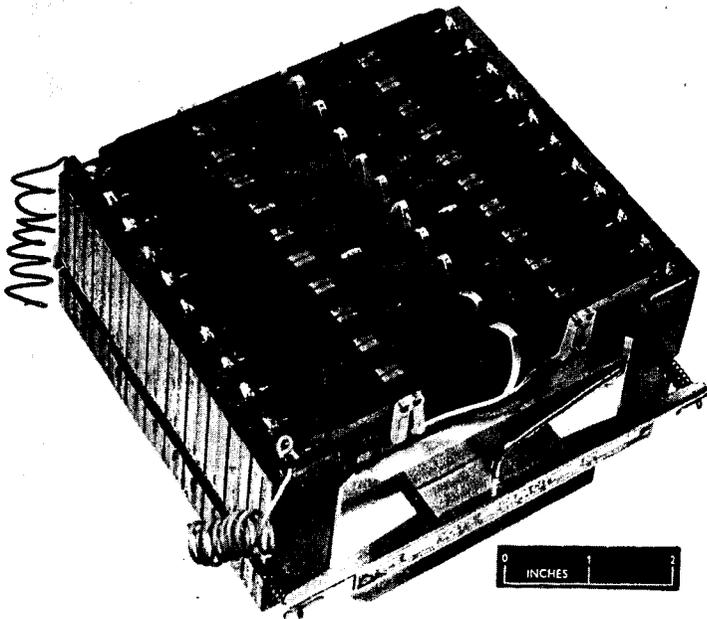


FIGURE 4 ECL LTD. Zinc/Air Battery

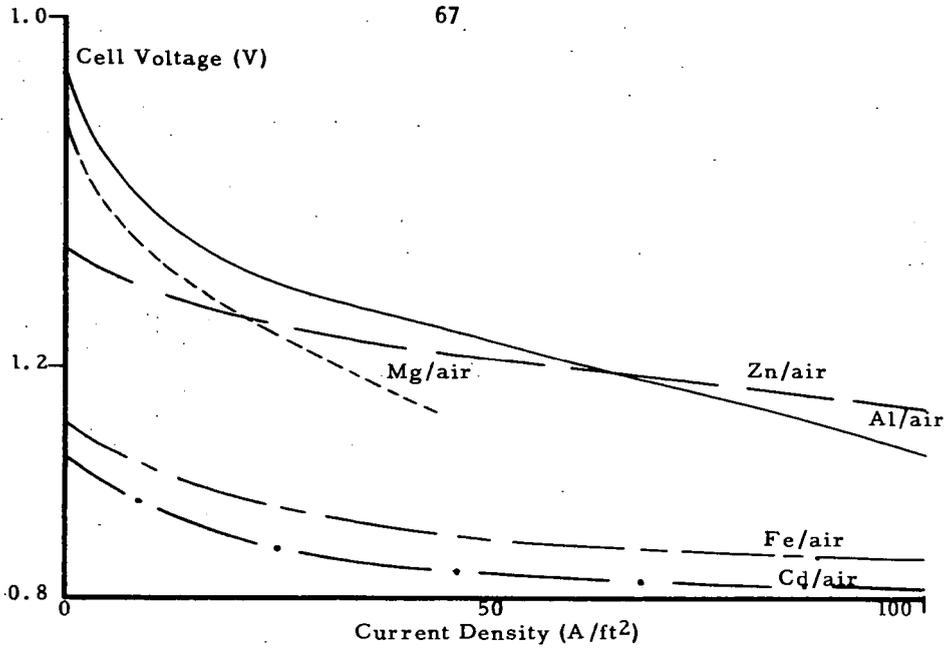


FIGURE 5 Polarization Curves of Zinc/Air Cells

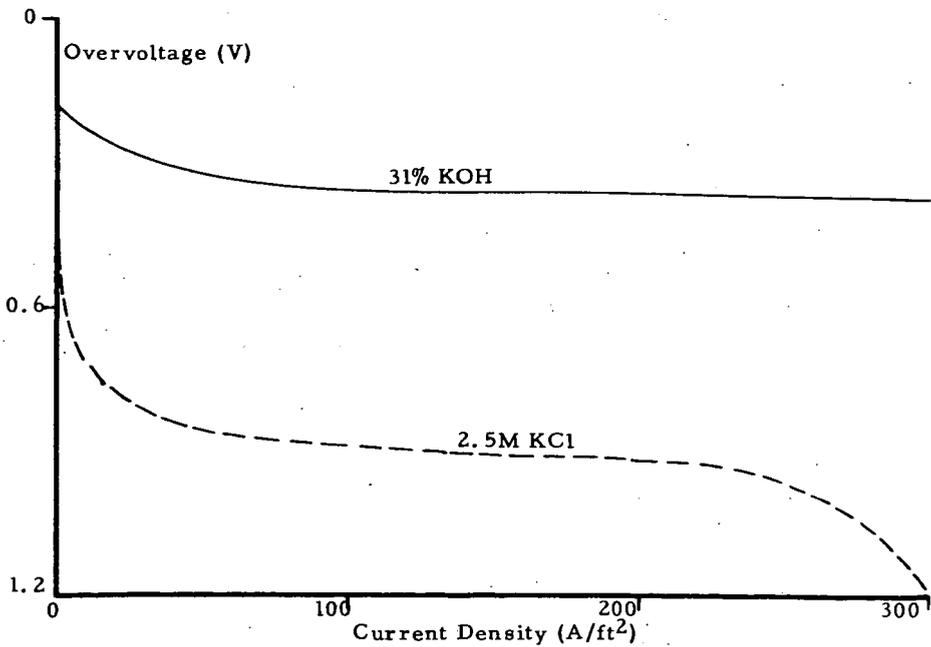


FIGURE 6 Cathode Polarization Curves in Alkaline and in Chloride Electrolyte

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