ZINC-AIR BATTERIES
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Good results have been obtained to date with zinc as the anode in primary zinc-air or zinc oxygen batteries. Zinc electrodes in thicknesses up to 1/4", are operating at 60% or better of theoretical efficiency with regularity. These batteries yield energy densities in the order of 80-150 WH/lb.

Either noble or non-noble metal catalyzed air or oxygen electrodes may be used for primary batteries. In general, Pt is used as the catalyst in "refuelable" batteries, while carbon, nickel, silver, and silver-amalgam are used for one-shot types. The general mode of operation for the one-shot battery is to add water to activate. However, it is more desirable to store the battery wet and activate by admitting air. For an air activated battery the storageability of the zinc electrode as well as the wetting characteristics of the air electrodes become important considerations.

Zinc electrodes must be heavily amalgamated to prevent self discharge and the evolution of hydrogen. The recrystallization properties of zinc and zinc oxide must be taken into account since crystal growth during long term stand, particularly at elevated temperatures, can partially passivate the zinc electrode. Therefore zinc electrode characteristics must be determined and controlled before activated storage zinc-air batteries are completely feasible.

In order to use the zinc-air system as a secondary battery one basic characteristic of zinc must be overcome. This is the fact that zinc, unlike other secondary battery electrodes such as Ni, Ag, Fe, and Cd, has a relatively high solubility in alkaline electrolyte. With oxidized zinc species being soluble. In addition, zinc tends to supersaturate the electrolyte during anodization to a value approximately 2 times the equilibrium value.

The high zinc solubility leads directly to such failure causing mechanisms, as zinc electrode shape change, dendrite growth and separator penetration, and the precipitation of zinc oxides in the air electrode.

"Shape change" is the loss of geometric surface area due to sluffing off and redistribution of zinc with cycling. This leads to the densification of the zinc metal formed on charge at the surface of the electrode, thus preventing full utilization of the remaining zinc oxide. Shape change

therefore results in a gradual loss of capacity and voltage with cycling until such time as the limiting current density is exceeded and then capacity rapidly falls below minimum levels.

Shape change tends to be more severe in secondary zinc-air cells than in Ag-Zn. This occurs because in the air system the zinc electrode is limiting on both charge and discharge. This causes the zinc to be fully worked each cycle rather than only 1/3 to 1/2 utilized as is the case in Ag-Zn. Therefore the shape maintenance effect of reserve zinc oxide is not available in Zn-air batteries.

Steps that can be taken to minimize shape change include the addition of binders. Particularly good results have been obtained with Teflon, as developed by the Yardney Electric Company (see reports on Contract DAAB07-67-C-0185). Minimization of the amount of amalgamation has also reduced shape change, although some Hg is required to prevent self discharge. Hg contents of the order of 0.5-1.0% appear optimum.

Another development from the Ag-Zn system that should prove useful in reducing shape change is the use of zinc electrodes having a larger geometric area than the positive electrodes. These oversized zinc electrodes appear to be effective in reducing edge effects which are points of higher potential and faster dissolution. Based on results obtained in silver-zinc cells it would appear that shape change can be minimized sufficiently to provide a life of more than 100 cycles, with 300 cycles a distinct possibility.

However, even if shape change is controlled the problem of separator penetration by zinc dendrite growth must be overcome if adequate cycle life is to be maintained. To date most of the conventional film type separators tested have not proved adequate. These include cellophane, fibrous sausage casing, poly (vinyl methyl ether/maleic anhydride) in a methyl cellulose base, and radiation grafted polyethylene. These materials have all been subject to oxidative attack by nascent oxygen or have high resistance which accentuates shape change. However, inorganic separator materials as developed by Douglas and more recently by other companies have shown promise as non-oxidative materials that are capable of preventing zinc penetration. Over 50 deep cycles have been obtained to date with these materials without failure.

Zinc dendrite growth may also be minimized by limiting overpotential on charge. Studies by McBreen have indicated that 70 mV overpotential above rest potential is sufficient to cause dendrite growth. Fortunately, zinc is a highly active electrode and does not reach this level except at the end of charge.
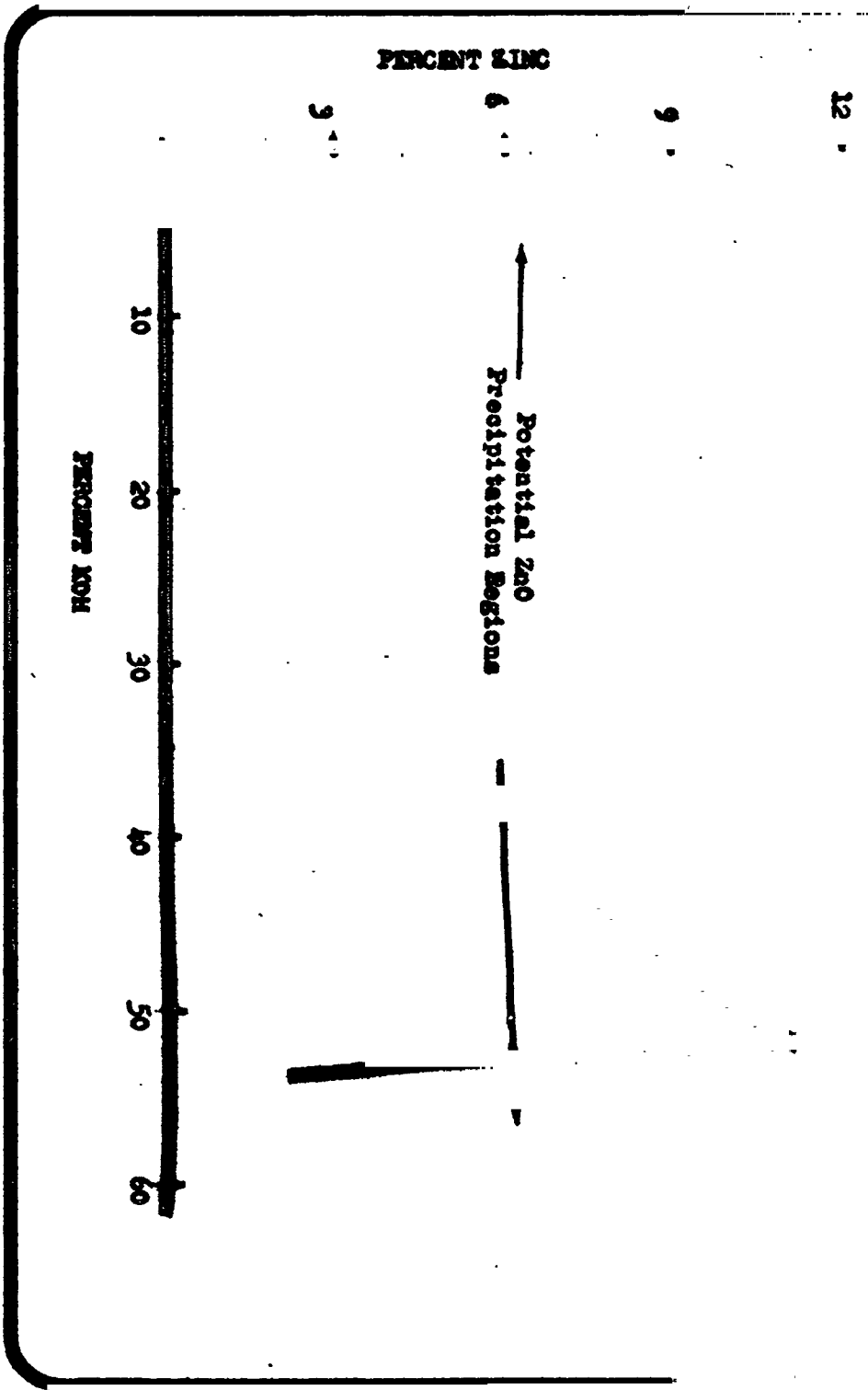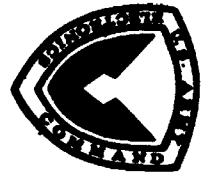
One failure mode that is unique to the Zn-air system is zinc oxide precipitation in and on the air electrode. The figure shows the solubility of zinc as a function of KOH concentration. Precipitation can occur at the end of charge when the electrolyte in the air electrode compartment is dilute from the generation of water. However, it is more likely to occur at the end of discharge when the electrolyte is very concentrated and large amounts of soluble zinc are available. The precipitation of zinc oxide in the air electrode is more likely to occur if a random cycling regime with long stand periods is followed rather than on rapid automatic cycling since rapid cycling tends to minimize the swings in electrolyte concentration. This leads to a critical current density for zinc-air batteries above which zinc oxide precipitation occurs, changing the wetting characteristics of the air electrode. This current density value may be considerably lower than the polarization behavior would indicate. However, this critical value is dependent on such factors as separator type, cycling conditions, and temperature, etc.

The air electrode for secondary zinc-air batteries appears to require the use of noble metal catalysts such as Pt, if auxiliary charging electrodes are to be avoided. This is desirable since it is calculated that, for a fixed volume, energy density will be reduced by approximately 1/3 if an extra charging grid is used.

To summarize, Zn-air secondary batteries appear capable of energy densities of 75-100 watt-hours/lb and can operate for 100 or more cycles using separators of the inorganic type. Much more work is required to optimize the air-zinc system and to determine its limiting use conditions.

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