

PIC-BAT 209/11

MAGNESIUM-AIR BATTERIES

by

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Among the anodic materials considered for use in metal-air batteries, magnesium ranks second only to zinc in characteristics deemed suitable for use in portable power supplies. From a theoretical point of view, magnesium would appear to rate higher than zinc, having both a higher thermodynamic potential and a higher calculated coulombic capacity per unit weight (Mg-1000 A.H./lb vs Zn-372 A.H./lb). However, practical considerations in past studies have shown that magnesium does not produce its theoretical potential in aqueous solutions and because of undesirable, and to some extent, uncontrollable side reactions does not provide its theoretical coulombic capacity either. For optimum use as a battery anode, magnesium should be used in solutions having a pH range from 6 to 9. Below pH 6, hydrogen formation becomes quite rapid and chemical corrosion consumes the major portion of the anode to the detriment of the electrochemical coulombic efficiency. Above a pH of 9, magnesium metal passivates through oxide or hydroxide film formation which acts as an insulating layer and electrochemical activity is inhibited severely.

There is, of course, no difficulty in obtaining solutions falling within the proper range of pH. General Electric Company pursued the use of sodium chloride solutions and achieved some measure of success at temperatures above freezing. The optimized solution of sodium chloride freezes at approximately 25°F. Prototype batteries were built and operated. Current levels were not as high as hoped for, and voltage transients produced some difficulties in achieving good voltage regulation in the battery. Excess water requirements also caused greater battery volume and weight than was originally estimated. These difficulties along with some component designs will require further investigation which could not be made under the time stresses of the original program. This work did point out the feasibility of a high rate, high energy density magnesium-air battery producing 50 watt-hours per lb.

In research studies for USAECOM, Yardney Electric Company, after a limited investigation of several salts, settled on use of a 3:2 eutectic of 4 N sodium-lithium perchlorate solution which was found advantageous in operation to -15°F. At -15°F, approximately 33% of room temperature capacity is obtained. Room temperature capacity approaches only 65% coulombic efficiency of the magnesium anode because of the corrosion resulting from chemical interaction of magnesium and water. At 125°F this undesirable

side reaction increases and only 40% of the nominal capacity is obtained. Figure 1 shows the effect of temperature on the cell voltage in the magnesium-air system using mixed perchlorate electrolyte.

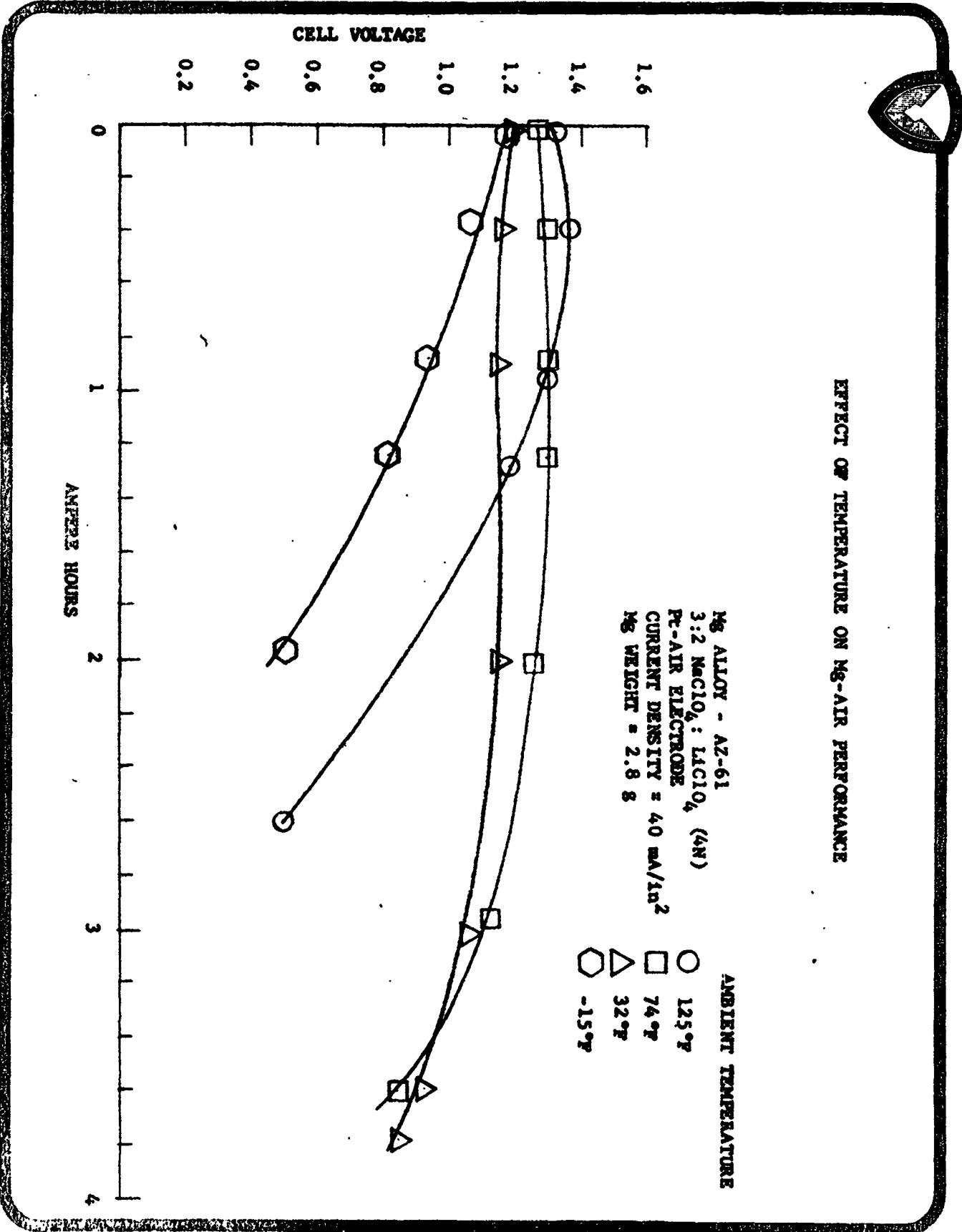
Current densities with the magnesium-air system are not as high as with the zinc system. Because of the resistivities of the electrolyte and the air cathode, and the use of sheet magnesium rather than the highly porous structure anode (as used in the zinc system) about 25-30 ma/cm² is optimum current density for efficient use in the magnesium-air system. Cell voltages of 1.24-1.28 volts are obtained at current densities of 12 ma/cm² (80 ma/in²). Figure 2 shows the effect of current density on the cell voltage in the magnesium-air system using perchlorate electrolytes.

In battery structures, the need for precise and proper designs is much more stringent in magnesium-air batteries than in zinc systems. Volume considerations especially must be viewed judiciously. The interelectrode spacing requirement, for example, was found to be 3 times the thickness of the magnesium sheet, i.e., the required interelectrode distance was 170 mils for a 55-60 mil thick magnesium anode. The large volume requirement is the result of the need for a much greater quantity of water in the magnesium system than for the zinc system. There is at least a threefold reason for the excess water requirement; to accommodate the voluminous reaction product (Mg(OH)₂) evolving from both electrochemical activity and from the uncontrollable chemical interaction of magnesium and water, to allow for the inherent water vapor evaporation through the cathode walls and, of course, to provide an ionic medium for cell reaction. It is mainly this excess of water that reduces the energy density of the magnesium-air system. Electrolyte in the magnesium system amounts to 80-85% of the weight of the active materials whereas in the zinc system only 30-35% is required for the electrolyte.

Despite the above difficulties these studies show that magnesium-air batteries can be produced having energy densities on the order of 50-55 watt-hours per lb.

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MAGNESIUM-AIR POLARIZATION

