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BRIEF INVESTIGATION OF AN ASYMMETRICAL ALTERNATING-CURRENT BATTERY-CHARGING TECHNIQUE

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BRIEF INVESTIGATION OF AN ASYMMETRICAL ALTERNATING-CURRENT BATTERY-CHARGING TECHNIQUE

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SUMMARY

A new battery-charging method using asymmetrical alternating current was briefly evaluated. This technique, invented by Ernst Beer of the Netherlands about 1954, was described by R. W. Hallows in reference 1.

Based on the experiences of R. W. Hallows and of Maurice F. Baddour of the Lewis Research Center, this technique has shown a capability of recharging some primary (Leclanche) batteries a large number of times. Some Leclanche batteries are still in regular use in spite of being in service for a period of 2 years.

A limited evaluation of this battery-charging technique was conducted with the following results:

1. This technique charged all batteries tested (Leclanche, alkaline, and lead-acid) to greater than their rated voltage. However, if placed on the shelf, these batteries self-discharged down to their normal voltage.

2. This extra voltage represented a 4 percent increase in energy density for the Leclanche type battery under conditions of a 150 milliampere discharge.

3. The technique showed some ability of recharging batteries from very deep discharges.

4. Batteries left on charge for as long as a week showed no permanent damage.

Although not specifically shown by this test, it is well known in the plating field that asymmetrical alternating-current plating can build up coatings at a much higher rate than can be done by conventional direct current. It is also known that the reverse-current part of this charging cycle will tend to act as a depolarizer. As a result, use of this technique should lead to significantly higher charging rates than obtainable by conventional dc-charging technique.

Furthermore, since this current cycle is similar to that used in electropolishing circuits, it is to be expected that the electrode material will be replated in smooth, even, hard layers. This should contribute to improved reliability and, hence, longer cell life in rechargeable batteries, since dc-charging techniques typically plate the electrodes with loose, spongy coatings. In actual practice this loose electrode material often falls off, causing cell deterioration and failure.

INTRODUCTION

An interesting item of technical information developed in the Technology Utilization Program was a report of a circuit which could recharge Leclanche cells (flashlight-type batteries) a great number of times (ref. 1). The possible recharging of these primary batteries has commanded a great deal of attention for many years within the battery industry. Typical systems existing today are direct-current chargers having a capability of recharging primary dry batteries a small number of times, probably less than ten. This new charging technique uses an asymmetrical alternating current and voltage in a manner similar to presently existing periodic reverse electroplating and electropolishing circuits. This technique incorporates certain physical principles (to be discussed later in this report) which theoretically show promise of permitting many cycle recharging of some primary batteries.

Potential NASA interest in such a charging system is derived from the observations that some primary batteries:

(1) Have a higher power density than space batteries presently used

(2) May be rechargeable within limits not yet completely defined

(3) Represent a much cheaper power source than presently used space battery systems.

Beyond these primary battery considerations, this circuit may be a more reliable, efficient, and faster way of recharging presently existing rechargeable space battery systems.

Accordingly, a limited experimental evaluation was made of this charging technique in order to help determine a future course of action.

BACKGROUND

Several years ago, Maurice F. Baddour, of the Lewis Research Center, constructed a charging system based on reference 1. Using this system he has been successfully recharging Leclanche batteries, some for as long as a 2 year period. The following information is based on discussions with him.

The only limitation found thusfar to battery life was not to allow a battery to discharge below a value of ≈1.45 volts (this value varies slightly with battery manufacturer). If the battery were allowed to discharge below this voltage value, holes appeared in the outer zinc electrode. These holes exposed the inner ingredients to the atmosphere, and allowed them to leak out and dry up, which ultimately resulted in battery failure. To date, no failure has been experienced, if the battery were recharged before holes appeared in the zinc case.

The physical processes behind this battery action seem to be as follows: In the discharge of an ordinary Leclanche dry-cell battery, the outer zinc electrode goes into solution by the (not universally believed) chemical reaction (ref. 2).

$$Zn + MnO_2 + 4NH_4^+ + 4Cl^- \rightarrow Zn(NH_3)_4^{++} + Mn^{++} + 4Cl^- + 2H_2O$$

In principle, this chemical reaction is reversible with the zinc being replated out of the solution. If this plating (recharging) process is carried out using direct current, the plating tends to deposit itself in an irregular fashion on the inner surface of the zinc can. This irregular deposition results from the internal electric field, due to charging, being greater on high points of naturally occurring irregularities; the result is a greater migration of zinc to these points and further accentuation of the surface irregularity. If the charge-discharge cycle is repeated several times, a hole is eaten in the outer-wall zinc electrode, and battery failure results. In the proposed charging scheme, the new circuit plates out the zinc material in a very regular fashion; therefore, as long as the battery voltage is not allowed to deteriorate to the point where holes appear in the case, the battery should continue to be rechargeable for a very long time.

Another observation was that a new 1.5-volt dry-cell battery could be charged to greater than 2.0 volts by this charging technique.

It has been suggested that in designing the charging circuit, best operation is achieved if the reverse current part of the asymmetrical wave is about 10 percent of the forward current.

From reference 1 it was learned that the device was invented about 1954 by Ernst Beer of the Netherlands. A check of the patent status showed that patent number 2,752,550 was issued to Ernst Beer on June 26, 1956. A copy of the patent is presently being acquired.

Reference 1 points out that Leclanche batteries have been used as secondary batteries for periods of time approaching 7 months without experiencing any troubles. Furthermore, it was calculated that at 250 milliampere drain, these batteries have put out approximately $37\frac{1}{2}$ to 40 ampere-hours while still apparently being in good condition. For purposes of comparison, ordinary dry-cell batteries under similar discharge currents contain 2 to $2\frac{1}{2}$ ampere-hours (ref. 3).

PROCEDURE

Based on the preceding information, a charger-tester was designed (fig. 1) and constructed.

A simple program was outlined to meet the following objectives:

(1) To determine if Leclanche primary batteries could be charged to greater than their rated voltage

(2) Presuming that they could be charged to this higher voltage, to measure any actual increase in energy density within the batteries

(3) To measure the voltage limits within which these batteries could be recharged

(4) To learn if this scheme could be applied effectively to other types of batteries

Most data on battery conditions were measured with a Simpson model 260 voltohm meter. The data should be taken as being approximately correct with a particular emphasis placed on trends rather than on absolute magnitudes.

RESULTS AND DISCUSSION

Leclanche Batteries

Bothe new and used D-type batteries were used in the tests. Furthermore, since the charger was designed to charge three batteries, unless specifically stated, any further reference in this report to a set of batteries will mean three D-type batteries.

A set of new batteries, each initially reading 1.5 volts, were placed in the charger and charged overnight. When checked the following morning each individual battery was found to read greater than 2.0 volts. To find whether or not this voltage increase represented a real increase in energy density, the discharge characteristics of these batteries were compared to that obtained by the discharge of three ordinary batteries. The tests were conducted holding a constant discharge current of 150 milliamperes. The results of this test are presented in figure 2. In addition, a set of batteries, individually discharged to $\approx$1.3 volts, were obtained. Examination showed that they had several small holes in their zinc cases. These batteries were placed in the charger where they were individually charged to 1.8+ volts; their discharge characteristics were then measured and are plotted in figure 2.

The data show that the extra voltage did produce some additional energy. The batteries discharged until they lost their excess charge; at this point they followed the discharge characteristics of the chosen typical, normal batteries. This added charge represents about a 4 percent increase in battery energy density (considering Leclanche batteries as having an energy density of $\approx$10 Whr/lb, ref. 3). If these supercharged batteries were placed on the shelf, they were found to self-discharge to their normal 1.5 volt condition in about 1 to 2 weeks. This would, however, pose no problem if the batteries were operated in a daily duty cycle.

In addition to the foregoing experiments, a number of miscellaneous observations were made.

On several occasions a set of batteries was left on charge for relatively long periods of time (at times for as long as a week). This long over-charge caused a slight lowering of the voltage of the battery and a lower charge level. If these batteries were discharged and then recharged they seemed to be restored to their supervoltage condition.

On two occasions sets of batteries were completely discharged. When recharging was attempted, it was found that these batteries would accept only a slight amount of charge. If, however, these partially recharged batteries were discharged slightly, and then again recharged, they charged to a higher voltage. If this charge - slight-discharge routine were carried out several times, the batteries could be restored nearly to normal voltage. It is not known what precisely is happening; however, if this situation is investigated it may show a technique of restoring batteries from very deep discharges.

Other Batteries

Because of extreme sensitivity to temperature and being limited to relatively low values of current output, Leclanche type batteries will probably not be considered for use in outer space. To determine the circuit-charging capability on other type batteries, three D-type alkaline batteries were purchased. Although rated at 1.5 volts, each of these batteries initially read 1.42 volts on the voltohm meter. The combination voltage of the three batteries installed in the battery charger read 4.4 volts.

The system was placed on charge and about $2\frac{1}{2}$ hours later, the combined voltage read 5.2 volts. At a total time of 3 hours and 40 minutes the voltage had declined to about 5.0+ volts. Continued charging to a total of 7 hours showed no further voltage change. When removed from the charger the individual batteries read 1.65, 1.62, and 1.62 volts respectively.

These batteries were discharged at a current drain of 400 milliampers. The results of th᷊ test are shown in figure 3. By extrapolation, it appears that the increased battery charge maintained the discharge current for approximately 40 minutes. This set of batteries was recharged and when removed from the charger, the individual voltage levels, in the same order as previously listed, were found to be 1.68, 1.68, and 1.67 volts. When allowed to sit on the shelf these batteries also self-discharged down to their rated voltage in about the same period of time as the Leclanche batteries.

To compare this charging technique with a commonly used technique, a fully discharged lead-acid battery was obtained. Although having been charged with a standard charger for long periods of time, this battery would show no more than 50 percent capacity by specific-gravity measurement, and, as a result, had been discarded. Repeated charge-discharge operations, using the new charging technique, restored this battery to 100 percent capacity (specific gravity) and a voltage reading of 2.20 volts. This battery self-discharged overnight to its normal value of 2.0 volts and a specific gravity equivalent to ≈90 percent of full charge.

While no conclusions can be drawn from this single case, it is known that the recharging circuit possisses the same type current characteristic as is used in electropolishing technique. It is therefore expected that this new charging technique, because of its ability to replate electrode material in smooth, hard layers (ref. 1), should contribute to improved reliability and longer life for presently used rechargeable batteries.

CONCLUSIONS AND RECOMMENDATIONS

As a result of receiving an interesting bit of information, a limited study and test program was conducted to evaluate an asymmetrical alternating-current battery-charging technique.

Based on the experiences of previous users, this technique has shown a capability of recharging some primary (Leclanche) batteries a large number of times. Some Leclanche batteries are still in regular use in spite of being in service for a period of 2 years.

Results of the test program showed:

(1) This technique was able to charge all batteries tested (Leclanche, alkaline, and acid) to greater than their rated voltage.

(2) The extra voltage was a real increase in energy density, amounting to a 4 percent increase for the Leclanche type battery under conditions of a 150 milliampere discharge. If placed on the shelf these batteries self discharged to 1.5 volts in approximately 1 to 2 weeks.

(3) This technique has some capability of recharging batteries from very deep discharges.

(4) Batteries left on charge for periods of time up to a week experienced no detectable permanent damage.

While not specifically shown by this test, it is well known in the plating field that periodic current reversal methods can plate coatings at a much faster rate than can be done by conventional direct current methods. It is further known that the reverse-current part of the charging cycle will tend to act as a depolarizer. Use of this technique should lead to significantly higher battery-charging rates. Furthermore, a problem with dc chargers is that the electrode material is plated on as a loose, spongy mass which often falls off and ultimately leads to battery failure. The current characteristic of this battery charger is similar to that used in electropolishing circuits and because of this characteristic, electrode material should be replated as a smooth, hard surface (ref. 1), thereby contributing to increased reliability and long life.

All in all this test has created more problems than it has solved. However, because of the large apparent potential in our space program, it is suggested that NASA initiate an in-house or contractor program to continue the evaluation and exploration of this charging technique.

REFERENCES

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3. Anon: "Eveready" Battery Applications and Engineering Data. Union Carbide Consumer Products Co.

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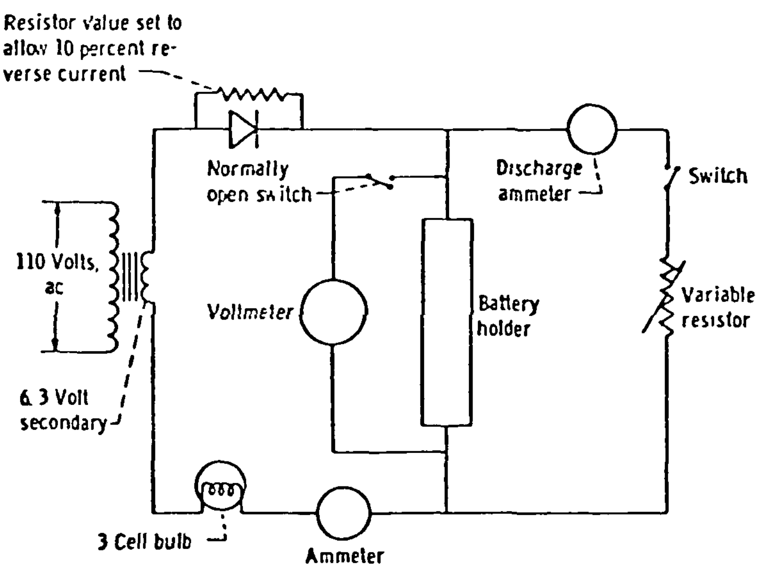

Figure 1. - Schematic diagram of battery charging circuit.

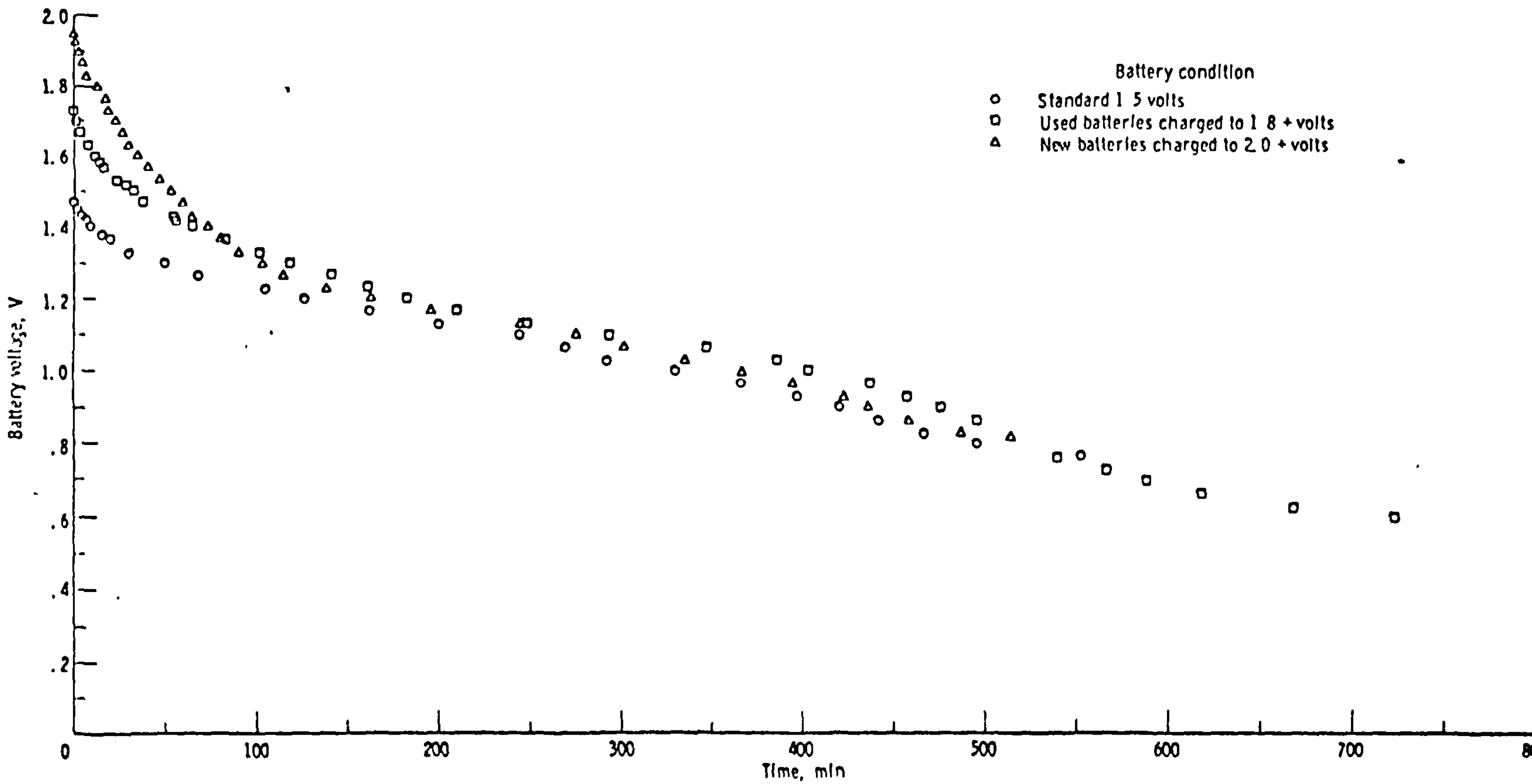

Figure 2. - Leclanche battery voltage variation at 150 milliampere discharge.

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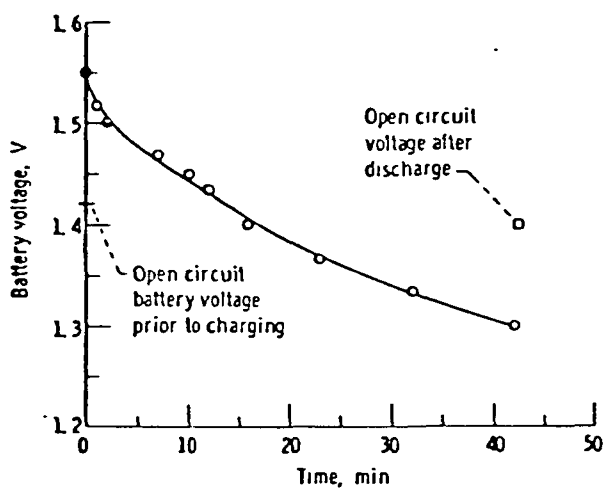

Figure 3. - Alkaline battery voltage variation at 400 milli-ampere discharge.