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20. Abstract

Thin film solid-state electrochemical cells with inorganic components were investigated. Various combinations of materials and fabrication techniques were studied and classified to determine which had the better chance for commercialization. Theoretical predictions were verified by experiments, and provide a sound basis for predicting promising combinations. These thermovoltaic cells are divided into 2 main categories; Large cells that are maintained at a high operating temperature by joule heat, and small or medium size cells that operate close to room temp. in a humid environment. Within these categories, there are primary and secondary type cells that offer distinct advantages over commercially available cells in both performance and price. High specific power(100watt/lb.)and specific energy(1000 watt-hr/lb) is achieved by eliminating weight of chemical oxidizers,massive electrodes and enclosures used in conventional batteries.

CERTIFICATION OF TECHNICAL DATA CONFORMITY

THE CONTRACTOR, Energy Innovations, Inc., HEREBY CERTIFIES THAT, TO THE BEST OF ITS KNOWLEDGE AND BELIEF, THE TECHNICAL DATA DELIVERED HEREWITH UNDER CONTRACT NO. DAAH01-86-C-0975 IS COMPLETE, ACCURATE, AND COMPLIES WITH ALL REQUIREMENTS OF THE CONTRACT.

April 30, 1987	Dr. Meredith C. Gourdine/President
DATE	NAME AND TITLE OF CERTIFYING OFFICIAL

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I. INTRODUCTION AND SUMMARY

1.1 Objectives

The original objectives of the Phase I research effort, as stated in the proposal that was funded, are given below:

1. To determine the optimum materials and methods of construction for single thermovoltaic cells:

   a. What is the best way of applying the oxide and graphite coatings?
   b. Can the present oxide coating materials be modified to achieve even lower resistivities?
   c. Can even thinner aluminum foil be used in the construction process?
   d. How thin can the oxide coating be made?
   e. How thin can the graphite coating be made?
   f. What are the performance characterisitics of the optimum single cell at elevated temperatures?
   g. Can the single cell be rapidly charged and discharged repeatedly without damage?

2. To determine the best method for constructing batteries of parallel stacked cells.

   a. What is the best way to bind the cells together?
   b. What is the best way to connect the cells in parallel?
   c. What is the best way to provide terminals at the top and bottom of the stack?
   d. What are the high temperature performance characteristics?
   e. What are the losses due to stacking?

3. To determine the best method of stacking in series the parallel stacked cells.

   a. How should the parallel stacked batteries be bound together?
   b. How should they be connected?
   c. What are their high temperature performance characteristics?
   d. Can we build a 12 volt battery having a volume 3" x 3" x 3" and delivering more than 100 watts or more and 10^3 watts/m^3?
   e. Can such a battery, when properly insulated maintain its own operating temperature?

Most of these objectives were met, with the notable exception that we were unable to build a cell that develops 100 watts within a volume 3" x 3" x 3". However, we now know that this is possible based on experimentally verified theory, and what we have learned about the selection of materials and methods of fabrication.

1.2 Approach

The report would be too tedious for the reader to follow if we presented our work in chronological order, or in the order suggested by the list of objectives, because we investigated such a large number of combinations of materials and methods of fabrication before determining which cells have the most promise, and in which particular applications. It is convenient for us to consider our research work divided into four distinct categories as shown below:

	HIGH TEMPERATURE DRY CELLS	LOW TEMPERATURE DAMP CELLS
3 COMPONENT CELLS	1 a. +(Graphite/Slip/Aluminum)-	3 a. +(Graphite coated paper/magnesium oxide powders/Aluminum)- b. +(Graphite coated paper/Aluminum oxide powder/Aluminum)- c. +(Graphite coated paper/Sodium Chloride in paper/Aluminum)- d. +(Graphite coated paper/Sodium Chloride in papers/Aluminum)- (wound) e. +(Graphite coated Aluminum/Sodium Chloride in Paper/Aluminum)- (wound)
2 COMPONENT CELLS	2 a. (Nickel paint/Slip/Nickel paint) b. (Nickel Chromium wire/Slip/Nickel Chromium wire)	4 a. (Graphite Coated Paper/Sodium Hydroxide in paper/ Graphite Coated Paper) (wound) b. (Copper/Furnace Cement in Paper/Copper) c. (Graphite coated paper/Sodium Chloride in paper/ Graphite coated paper) (wound)

1.3 General Results

A. Underlying Theory

The underlying theory is summarized in Section 2, where it is generally corraborated by presenting experimental evidence. The formulas presented there for specific power and specific stored energy provide a basis for selecting materials and methods of construction that can result in large cells and batteries with performances superior to existing cells and batteries, as shown in Figure 6. In particular, there is the possibility for exceptionally high specific stored energy because thermovoltaic cells and batteries do not require a large dedication of weights towards electrode and containment structure; the thin laminations of electrodes and separator material provide all the structure that is necessary. The main conditions for achieving high specific power are thinness of the laminations and low resistivity of the separator, and this can be achieved by special fabrication techniques and careful selection of separator material.

B. Category 1

After many unsucessful attempts, we built one cell in this category that lasted for several days as it discharged and oxidized aluminum foil at 1100°F. However, when we attempted to recharge the cell, we oxidized the graphite and formed CO_2, so this cell is not reversible. To make it reversible, we would have to replace the graphite by a noble metal, which would be too expensive. In its present form, it could serve as an excellent primary cell with specific stored energy in excess of 1000 watt-hr/lb. Its open circuit voltage was .67 volts, and its specific power was 4.29×10^{-2} watts/lb. THe oxide separator was a commercial ceramic, slip, which had one of the lowest resistivities of any of the oxide combinations that we considered; plus, it was the easiest to apply. By using thinner laminations in the future, the power density could be increased by as much as a factor of 40. (17.2 watts/lb).

C. Category 2

The cells in this category were built with only two components. The third component, a metal film, was induced by charging the cell and displacing oxygen across the oxide separator. During the discharge phase, oxygen ions travel across the separator and oxidize this third component. We describe in detail two cells in this category. We present information about the variation of performance with temperature and the ability to be repeatedly charged and discharged. The power density in cell B at 1800°F. was 1.27 watts/lb. With the possibility for making thinner laminations, we could achieve 100 x this value (1.27 watts/lb). The discharge period was 12 hours and the specific stored energy was 1.02 watt-hr/lb, which could have

been considerably greater if we discharge the cell longer. This type cell if properly fabricated on a larger scale would be ideally suited for making vehicle batteries, or for load levelling batteries, that would be charged and discharged on a regular basis.

Although the small prototype cells described in category 1 and 2 require furnaces to maintain their operating temperatures, in sizes above 100 watts the joule heat could maintain the operating temperature with only a small amount of thermal insulation. With larger batteries, the problem would be to remove the heat in order to prevent the temperature from getting too high.

D. Category 3

We found that we could operate close to room temperature, and achieve reasonable specific power and specific stored energy if the separator was kept damp by operating in a humid environment. Cells A and B demonstrated a disadvantage in that the voltage steadily decreased during the discharge; however, cells C and D did not. Cell C had a specific power of 1.65 watt/lb, and a power density of 4.46 watts/m^3. The discharge was for several days before we noticed holes in the aluminum foil, this cell was not able to be recharged. The specific stored energy for this period was 167 watt-hr/lb, but if the discharge were allowed to continue, it would have been much greater. Cell D is a hand wound version of cell C, and performed quite well, except that its resistance was somewhat higher than expected. This is traced to the fact that the graphite coated paper has a resistance much higher than the damp sodium chloride paper used as the separator. This can be corrected in future work and wound cells appear to be the easiest and least expensive to build.

Cell E is essentially the same as Cell D, except that the graphite coated paper is replaced by graphite coated aluminum to reduce the resistance in the graphite electrode. As a result, the specific power is increased from 1.65 watts/lb to 9.27 watts/lb, and the power density is increased from 4.46 watts/m^3 to 4.32×10^4 watts/m^3. Although we did not actually build Cell F, previous experience with Copper in place of Graphite suggests that we would get a stable cell with similar performance except for the increase in density and cost of copper as indicated in Table 2.

We built a machine for winding such cells and wound one like Cell 2D, 5" in diameter and 4" wide with open circuit voltage of .720 volts, and specific power of 5.71×10^{-2} watts/lb. At 500 watt-hr/lb, batteries of this type should find use when fully developed as inexpensive primary, or throw away batteries. Of course, the specific power and specific stored energy would increase substantially if we replace the graphite coated paper with copper, which we learn at the end of this project, is available as thin as .0007" at $28.00/lb.

E. Category 4

Cells A and B in this category were dissappointingly poor performers; however, Cell C (Copper/Furnace Cement in Paper/Copper), the last few days of the project, confirmed theory, and showed promise for further development. It was rechargeable, and has a specific power of 1.28 watts/lb, and a power density of 2.54×10^4 watts/m^3.

1.4 Conclusions

Based on the research performed in Phase I, we must conclude that the cells and batteries of categories 2 and 3 are the most promising for future development. The cells in Category 1 have the least promise of all because they used aluminum foil as the negative electrode, and aluminum has a melting point of 1250 degrees F. We have not been able to find a high temperature separator with a resistivity low enough at this temperature to provide sufficient specific power. There are other difficulties, but this one seems insurmountable at this stage of research. The first cells we built in category 4 were disappointing performers. For one reason or another, these cells either failed to take a charge or to hold a charge long enough to be of practical value. We suspect that it is because we had not perfected a good technique for inducing the third component, or negative electrode. During the last few days of this project, we apparently solved this problem by building Cell C (Copper/Furnace Cement in Paper/Copper). It proved to be rechargeable, and quite stable, comparing favorably with commercially available secondary cells.

Cells in category 2, high temperature dry cell with two components, also took a charge and held it well. The problems here are engineering problems associated with operating at very high temperature, above 1400 degree F. The development of large practical cells and batteries will require great deal of work on material selection and fabrication techniques. However, there is much technology that can be borrowed from development of high temperature batteries and fuel cells. There is ample reason to proceed because Phase I results indicate that very high specific power (over 100 watts/lb.) can be achieve with relatively inexpensive materials. There was insufficient time during Phase I to demonstrate how many charge-discharge cycles was possible, but with proper construction, there seems to be no theoretical limitation. Since this type battery must generate sufficient joule heat to maintain its high operating temperature, only large cells and batteries (over 100 watts) are feasible.

On the other hand, the cells of category 3, low temperature humid cells with 3 components, must be build in small sizes, because joule heat must be removed to keep the temperature low enough to maintain the humidity necessary

for low resistivity in the separator. Large batteries would consist of smaller units whose services must be continuously cooled by water or air. Phase I research has demonstrated that such cells have a specific stored energy much larger than conventional cells (over 500 watt-hrs/lb.at maximum power output),and , of course, they have much larger specific stored charge over 500 ampere-hrs/lb. The graphite coated aluminum/aluminum cell has also demonstrated a specific power of 10 watts/lb. Unfortunately, earlier tests were done with graphite coated paper/aluminum, and the coated paper had much more resistance along its length than the coated aluminum; we think this contributed to the oxidation of the aluminum from one end rather than uniformly across its surface. There was insufficient time to determine whether the cell with graphite coated aluminum eliminated this problem. If it has, then the cell maybe rechargeable. We also considered replacing the Graphite coated Aluminum with Copper to get better stability, as shown in Table 2. As shown in the following summary tables, formed from informations collected and presented in Appendix 4:

TABLE 1

RECHARGEABLE BATTERIES
(Secondary)

TYPE OF CELL	TYPICAL PERFORMANCE	WATT-HR/LB.	WATT/LB.	DOLLAR/WATT-HR	DOLLAR/WATT	DOLLAR/LB.	LB/IN^3	WATT/m^3
Lead Acid	480 watt-hrs. at 12volts and 2 amps, 24 watts, 28.2 lbs. 600 inch cube 71.9 dollars	17.0	.851	.15	3.0	2.55	.047	2.45×10^3
Nickel/Cadnium	460 watt-hrs at 12 volts and 9.2 amps, 110 watts, 144 lbs.,$460.00, 460 cubic inches	3.2	.764	1.00	4.18	2.68	.313	1.46×10^4
Nichrome/slip/Nichrome (1800 deg.F)	V_0 = .65 volt R_i = 80.6 watt w =3.74×10^{-5} lb v = 4.24×10^{-4} ft^3	500	140	.20	1.40	100	.0992	7.55×10^5
(Copper/Furnace Cement in Paper/Copper)	V_0 = 1 volt R_i = 100 ohms w = 1.95×10^{-3} lb v = 6×10^{-3} ft^3	500	1.28	.056	21.9	28	.325	2.54×10^4

TABLE 2

THROW-AWAY BATTERIES
(Primary)

TYPE OF CELL	TYPICAL PERFORMANCE	WATT-HR/LB.	WATT/LB.	DOLLAR/WATT-HR	DOLLAR/WATT	DOLLAR/LB.	LB/IN^3	WATT/m^3
Zinc/carbon D cell	9 watt-hrs at 1.5v 60 milliamps, 90mw, .209lb., .90 dollars, 3.46" ^{3}	43	.43	.10	10	4.5	.059	1.55×10^3
Alkaline Manganese D Cell	20w-hr at 1.5v and 130ma, 195mw 3.54"^{3}, .29lb., .49 dollars	.69	.65	.025	2.5	1.7	.014	5.57×10^2
Lithium/Sulfur Dioxide D Cell	23.2w-hr at 2.8v and 1.75amp, 4.90w .176lb., 3.22"^{3} 15.8 dollars	132	27.8	.68	3.4	4.90	.0546	9.28×10^4
Lithium Thionyl Chloride D Cell	36w-hr at 3.6v 1.1amp., 3.96w .218lb., 3.3"^{3}, 1.04 dollar	165	1.80	.29	.263	4.77	.0661	7.29×10^3
+(Graphite coated aluminum/ Sodium Chloride in paper/aluminum)- V_o = .67 volt R_i = 5 ohms w = 2.42×10^{-3} lb V = 6.6×10^{-2} .3		500	9.27	.016	.827	8	.0367	2.08×10^4
+(Copper/Sodium Chloride in Paper/Aluminum)- V_o = .67 volt R_i = 5 ohms w = 4.84×10^{-3} lb v = 6.6×10^{-2} .3		251	4.64	.087	3.89	19	.0734	2.08×10^4

Considering the fact that our low temperature humid cell can operate from freezing temperature up to 212 °F, and much higher if pressurized, and that commercial cells degrade rapidly at temperatures over 150°F, this provides another distinct advantage, in addition to much lower cost. For use as a primary, or throw-away, battery, the $^{+}$(graphite coated aluminum/NACL in paper/aluminum)$^{-}$ cell is ready for commercial development, provided that an impervious Graphite coating can be put on the Aluminum; otherwise, Copper could be substituted. Further research must be done to determine whether or not it is rechargeable, or can be made rechargeable. In its wound form, cells can be conveniently stacked in series to obtain any desired voltage. Individual cells must be small enough to be air or water cooled so the temperature does not become excessive, and drive off the humidity necessary for low internal resistance.

For applications requiring large batteries and high specific power, the cells of category 2 appear attractive compare to commercial cells and batteries. It must be large (over 100 watts) so that joule heat will maintain a sufficiently high operating temperature. This type battery is probably the best candidate for driving vehicles.

1.5 Recommendations

As a follow-on to Phase I research, it is recommended that:

1. The $^{+}$(Graphite coated aluminum/sodium chloride in paper/aluminum)$^{-}$ and/or $^{+}$(Copper/Sodium Chloride in Paper/Alumium)$^{-}$ cell be developed for commercial use as small and medium sized primary cells that can be conveniently stacked in series to form batteries of any desired voltage. These cells can be wound in small sizes (a,b,c,d), or custom wound in larger sizes for special applications.

2. The same cell should be studied to see if they are rechargeable or what has to be done to the aluminum foil to make it sufficiently homogeneous that it oxidizes uniformly across its surface, rather than forming pinholes.

3.More research should be done on the cells of category 4, low temperature damp cell with 2 components, in particularly, the wound cell (Copper/Furnace Cement in Paper/Copper)

4.The cells of category 2, high temperature dry cells with 2 components, should be developed as large secondary cells necessary for vehicle batteries. The emphasis should be on solving engineering problems like material selection and fabrication techniques to achieve the most cost effective batteries.

II. UNDERLYING THEORY

Figure 1 is a schematic of +(C/Al_2O_3/Al)- cells stacked and connected in parallel. A single cell consists of a sheet of aluminum foil that is entirely coated with a thin oxide material, except for its left edge. Then, on top of it, is another sheet of aluminum foil that is entirely coated with graphite and oxide, except for its right edge. The cell exists between the two sheets of aluminum foil, and shorting between the aluminum and graphite is avoided because it is unlikely that pin holes in two oxide coatings would coincide. Also, the width of the graphite coated foil is slightly less than that of the other foil in order that their edges do not coincide.

The left edges of the aluminum are connected together by graphite paint and this is extended over the top of the stack to form the negative electrode. The right edges of the aluminum foil that is coated with graphite are also connected together by graphite paint and extended over the insulation on the bottom of the stack and this forms the positive electrode. These parallel stacked cells can then be stacked in series to obtain batteries of any desired voltage.

The cells in all four categories obey the same general theory which is derived in considerable detail in appendix 1. For convenience, the most useful relationships for designing thermovoltaic cells and batteries are summarized below.

2.1 Open Circuit Voltage

The open circuit voltage or EMF, is due to the difference in oxidation potential, or free energy released by oxidation, at the dissimilar metal interfaces with the oxide separator. Figure 2 is a plot of ΔG^o vs. T for various metals, and for any dissimilar metals (1,2), then the open circuit voltage is

$$V_o = 1.06 \times 10^{-2} (\Delta G^o{}_2 - \Delta G^o{}_1) \qquad (1)$$

where $\Delta G^o = \Delta H^o - T\Delta S^o$ (2)

and ΔH^o is the difference in enthalpy associated with oxidation, and ΔS^o is the change in entropy due to oxidation. Using the first and second laws of thermodynamics, it can be shown that any electrochemical cell obeys the Gibbs-Helmoltz equation.

$$V_o = V_o{}^o + \beta T \qquad (3)$$

where $V_o{}^o$ is the voltage that would occur hypothetically at $T = 0^o$ K, and is due to chemical energy, and the temperature coefficient is

$$\beta = d V_o/d T \qquad (4)$$

and is due to conversion of thermal energy into electricity. The thermovoltaic cells tested in all four categories had $\theta > 0$ like that shown in Figure 4. This makes it feasible to save energy by recharging cells at a lower temperature than their discharge temperature because the back EMF during charging would be less. The extra energy would be coming from the thermal energy of the environment.

2.2 Current-Voltage Relationship

When a resistance is connected across the cell having internal resistance R_i, the voltage across the cell is given by

$$V = V_o - I\ (R + R_i) \qquad (5)$$

Thus, there is a linear relationship between V and I, the current, provided that R_i is independent of I. This is generally found to be the case, as evidenced by the typical straight load line for V vs. I as shown in Figure 3. This is not generally true for conventional electrolytic cells or high temperature cells designed to have extremely high current densities (current/area). In fact, it is high current density that limits the useful life of conventional cells, causing physical and chemical deterioration of the interfaces. In thermovoltaic cells, the current density is severely limited by the internal resistance of the separator, so if desired, large over voltages can be applied without damaging the cell. To achieve high current, thermovoltaic cells require large surface area, and this is achieved by using thin films within a given volume.

2.3 Short Circuit Current

The short circuit current is

$$I_s = V_o/R_i \qquad (6)$$

which clearly indicates how the internal resistance limits the current that can pass through the cells.

2.4 Internal Resistance

The internal resistance of the cell can be written in terms of the resistivity of the separator material, σ ; e.g.

$$R_i = \sigma\ S_o/\ A \qquad (7)$$

where S_o is the thickness of the separator and A is the area. It has been shown experimentally that for the dry cells, the resistivity obeys the relationship

$$\sigma\ /\ \sigma_\infty = R_i/R_\infty = \mathrm{EXP}\ (e\ V_g/k\ T) \qquad (8)$$

where the subscript infinity corresponds to the hypothetical conditions at $T = \infty$, e is the charge on an electron, V_g is the equivalent of the band gap voltage of a semiconductor, k is

Boltsman's constant. Figure 5 is a typical plot of log R_i vs. 1/T. The fact that it is a straight line verifies the theoretical model. The intercept with the vertical axis determines in this case that $R_\infty \approx 1\Omega$, and the slope of the line determines that $V_g \approx 0.7$ volts. The oxide separator in this particular example was slip, which is a mixture of oxides approximately in the proportions shown below.

Slip (Ball Mud and Talc)

Ball Mud:

SiO_2	58 %
Al_2O_3	27 %
TiO_2	1.5%
Fe_2O_3	.9%
CaO	.4%
MgO	.4%
K_2O	1.5%
Na_2O	.3%
LOI	10.1%

Talc:

SiO_2	61.5 %
Al_2O_3	.45%
Fe_2O_3	.2 %
MgO	26.2 %
CaO	4.83%
SO_2	.03%
K_2O	.33%
NaCl	.03%
LoI	7.07%
Acid Solid	4.6 %

Reference to textbook on semiconductor properties would show that these oxides in a regular lattice would have band gap voltages in excess of 3 volts. Separators we constructed were not regular lattices, but tiny particles of the oxide bound together by small amounts of binding material like glass. In other words, there were an extremely large number of dislocations rather than a regular lattice. This may account for the substantially reduced band gap.

We also know that electron thermally kicked from the valence band into the conduction band must attach themselves to oxygen to form oxygen ions that are responsible for the electrochemical action of the cell. Placing such a cell in a vacuum chamber, and removing the oxygen, thereby removes the voltage. Details about how oxygen ions move through an oxide separator are not known. They could be moving through the bulk material along the surfaces of the particle or through voids between the particles, or all three. Nevertheless, this model is obeyed without exception.

Some oxide separator and mixture of oxide have lower resistivity than other, but no clear pattern has yet been determined. Pure silicon dioxide powder as found in cab-o-sil

has a much higher resistivity than either alumina or magnesia in powder form, but mixtures like slip, or furnace cement (alkaline silicates), tend to have the lowest resistivity. There is also the possibilty that doping these oxides with donor impurities will further reduce the band gap voltage just as it does in semiconductors with regular lattices.

The mathematical model for the resistivity of the separators in damp cells is not known. We have determined that the purpose of the dampness is primarily to reduce the resistivity. When a cell is put in a dryer, its resistance increases but its voltage remains. However, when oxygen is removed by a vacuum, the voltage disappears. The voltage returns as oxygen is reabsorbed, and the resistance decreases as dampness is restored. Sometimes, with a paper separator, the voltage also increases somewhat when the paper is dampened. If additional ions are added to the water by dissolving acids, bases, or salts, the resistivity is further reduced, again without a large change in the open circuit voltage, but the the choice of additives to the water must be such that the materials in the cell are not chemically degraded. We found that acids and bases were too corrosive with aluminum in the cell, but sodium chloride was fine. We also found that if there was too much liquid in the separator, the chemical reactants at the interfaces are redissolved or precipitated or washed away, and the cell behaves more like an ordinary electrolytic cell. However, if the separator is merely damp, and there is plenty of oxygen in this porous media, the reactants at the interface remain in place, and the cell behaves like simple oxidation and reduction is the primary driving force, with all reactants remaining in place. We found that resistivity decreases some with temperature, but the main factor is still dampness.

2.5 Specific Power

The specific power of the cell is its power output per unit mass, and is given by the formula

$$P' = P/\bar{\rho}AS = V^2/R\bar{\rho}AS = (V_o^2/\bar{\rho}\,\sigma\, S_o S)\; R\, R_i/(R + R_i)^2 \qquad (9)$$

This shows that as the load resistance R varies from 0 to infinity, the power density goes from 0 to 0 having a maximum where $R = R_i$. It also shows that to design a cell to have a large power density, the following should be done:

a. Choose very dissimilar metals to increase V_o
b. Choose low density materials to decrease mean density $\bar{\rho}$.
c. Decrease resistivity of the separator by operating dry at high temperature, or damp at low temperature.
d. decrease separator thickness S_o
e. decrease overall cell thickness S

2.6 Specific Stored Charge

Thermovoltaic cells can be built with the oxidizer and the oxidant both hermetically sealed within the cell; however, since these cells will be operated in air, and it is difficult and costly to build hermetic seals, all of the cells we investigated could breathe in the oxygen it needed. Not having to store oxygen greatly reduces the weight of the cell as the following formula shows.

$$Q' = \frac{\text{stored charge}}{\text{mass}} \tag{10}$$

$$= \frac{\text{charge of an oxidant molecule}}{\text{mass of an oxidant molecule}} \cdot \frac{\text{mass of oxidant}}{\begin{array}{l}\text{mass of oxidant}\\ +\ \text{mass of oxidizer}\\ +\ \text{mass of separator}\\ +\ \text{mass of positive electrode}\\ +\ \text{mass of structure}\end{array}}$$

Unlike conventional electrochemical cell, thermovoltaic cells have essentially no mass of structure. This is the main reason that it has larger specific power, specific stored charge, and specific stored energy than conventional cells. If the cell is the type that breathes, then there is no stored oxidizer and the formula reduces to

$$Q' = \frac{\text{charge of an } O_2 \text{ atom}}{\text{mass of an } O_2 \text{ atom}} \cdot \frac{\text{molecular wt. of } O_2}{\text{atomic wt. of oxidant} \times \text{valence of } O_2/\text{valence of oxidant}}$$

$$\cdot \frac{\text{mass of oxidant}}{\text{mass of oxidant + mass of}^{+}\text{ electrode + mass of separator}}$$

$$= \frac{10^8}{8} \cdot \frac{16}{\text{atomic wt. of oxidant} \times 2/\text{valence of oxidant}} \cdot \frac{\rho_- \; S_-}{\bar{\rho} S}$$

where ρ_- is the density of the oxidant electrode, $\bar{\rho}$ is the mean density of the material of the cell, and S_- is the thickness of the oxidant (or negative) electrode while S is the total thickness of the cell. Hence, to achieve large specific stored charge we tried to do the following:

a. Choose an oxidant with a large valence; e.g. Al^{+++}
b. Choose an oxidant with as low an atomic weight as possible.
c. Make the relative thickness of the negative electrode, or oxidant, as large as possible; i.e. $1/2 < S_-/S < 1$.

For example, if $S_- / S \approx .75$, and the negative electrode is Al^{+++} and with atomic wt. 27, $Q' \approx 8.33 \times 10^6$ coulomb/kg = $.31 \times 10^3$ ampere hours / kg = 1.05×10^3 ampere hours/lb. Because of the large weight invested in the structure of conventional cells, and the storage of the oxidizer material, specific charge is more than 10 times lower than this value.

2.7 Specific Stored Energy

The specific stored energy of a cell is its specific stored charge times the voltage at which it will be discharged; i.e.

$$E' = Q' V = Q' V_o R/(R + R_i) \qquad (11)$$

Hence, if we discharge the cell at $V \approx 1$ volt, $E' \approx 1.05 \times 10^3$ watt-hr/lb., which again is more than 10 times that of the best commercial cells because of the large amount of weight invested in structure and oxidizer storage.

This is shown clearly in Figure 6 which is the plot of specific power vs. specific energy for various commercial and high temperature cells now under development. It includes curves representing the performance of air breathing thermovoltaic cells with very thin positive electrodes ($S_+/S << 1$) so that $\Delta_o \approx - \Delta S_-$. Each curve corresponds to a particular value of S_o and S while R is varied from 0 to infinity, the peak occurring where $R = R_i$.

2.8 Discharge Time

The time required to fully discharge a cell through a given resistance is given by

$$T \approx Q'/P' \qquad (12)$$

There is a formula derived in Appendix 2 that relates the relative increase in oxide thickness to the time of discharge and it is shown in Figure 6, a pair of discharge paths for the thicker cell (bottom two curves) and the thinner cell (top two curves). The thicker cell discharges in 10 hours while the thinner cell discharges in 7 hours. One discharge path is between peaks of the curves where $R = R_i$ while the other discharge path is at a constant power, requiring that R be reduced at the appropriate rate to maintain this condition.

2.9 Thermal Effects

It is shown in Appendix 1 that large batteries generate sufficient joule heat to maintain the desired operating temperature for dry operations. In fact, very little thermal insulation is required because heat is generated per unit volume, while it is removed per unit area. One advantage of using high temperature batteries is that it can transfer joule heat to air or water with much less heat transfer surface required. Furthermore, the resulting temperature of the cooling media could be high enough to achieve good thermal efficiency in heat engines.

Large low temperature damp cells have to be maintained at this temperature by cooling with air or water and this heat can be used for providing hot water or space heating.

It is shown in Appendix 3 that we can take advantage of the increase in open circuit voltage with temperature to increase the efficiency of operating rechargeable thermovoltaic cells. By discharging at a higher temperature and recharging at a lower temperature and EMF, less energy input is required than that extracted, the difference coming from the thermal energy in the environment. This is reflected in the following formula for efficiency:

$$\eta = \frac{\text{electrical energy out}}{\text{electrical energy in}} = \frac{V_o\,(1 - \Delta V_o/V_o)}{V_o'\,(1 + \Delta V_o'/V_o')} \qquad (13)$$

where the ′ denotes charging conditions, and if $V_o > V_o'$ because $T > T'$, this increases η, for given values of $\Delta V_o/V_o$ and $\Delta V_o'/V_o'$, which are the relative discharging under-voltage and the relative charging over-voltage, respectively.

III. SINGLE CELL EXPERIMENTS

3.1 High Temperature Dry Cells With 3 Components

a. $^{+}$(graphite/slip/aluminum)$^{-}$

This cell was constructed by painting a high temperature resistant microscope slide (1" x 3") with graphite in water having a K-sil binder. A sheet of aluminum was glued to another glass slide using the K-sil binder. A layer of slip approximately 1 mil thick was painted on the aluminum and cured and the two were sandwiched together overlapping at the end approximately 1/4". Brass wires were mechanically secured to these tabs while electrical connections were made with graphite paint and the entire assembly was encapsulated with slip. For additional strength, some furnace cement was used as bands around each end. The cell was hung in a small furnace and operated at a temperature approximately 1100°F. The cell was allowed to discharge through a resistance of 10,000 ohms, and the voltage was recorded by our computer. Initially we measured the open circuit voltage V_o, and the voltage V across a load resistance R, and determined the internal resistance of the cell from the formula $R_i = R\,(V_o/V - 1)$. Experience allowed us to assume that R_i remained constant during the test, so the computer used the same formula to calculate V_o as it decreased with time. The computer printouts for V_o and V in this test are given in figures 7 and 8.

The test lasted 138 hours, or approximately 6 days, and ended abruptly when the brass wires broke after being oxidized through. After the cell cooled, inspection showed that most of the graphite had disappeared, having been oxidized and turned into CO_2. The graphite in the electrical connection was still intact, suggesting that graphite in the cell may have been forced to oxidize when we tried to recharge the cell by driving the current in the opposite direction with an external power supply. Graphite will oxidize in air at temperatures above 800°F. very rapidly, but as long as the cell is discharging, whatever oxygen is breathed into the cell would be charged on the graphite, diffuse across and oxidize the aluminum. When we reverse this process the field can push the oxygen ion into the graphite and form CO_2 gas at this high temperature.

The aluminum foil was also oxidized and there was a white powder remaining that was probably aluminum oxide.

We conclude that this type cell can only be used as a primary cell because the graphite will disappear during recharge. The weight of the active ingredients in this cell was approximately 2×10^{-4} Kg = 4.4×10^{-4} lbs. Typically the open circuit $V_o \cong .67$ volts and $V = .435$v across $R = 10^4\,\Omega$ so Power $= V^2/R = 1.89 \times 10^{-5}$ watts, therefore, the specific power was 4.29×10^{-2} watts/lb. The typical internal resistance recorded was $R_i = 5.4\text{k}\Omega$,

and the area of the cell is $\approx$ 1" x 2" = $2.29 \times 10^{-3} m^2$. Assuming that the thickness of the slip is $\approx$ 4 mils = 10^{-4} m, the resistivity of the slip is $\rho \approx R_i A/S_o = 1.17 \times 10^{-5} \Omega$ - m. The energy released by the cell is E $\approx 2.16 \times 10^{-5}$ watts x 138 hrs = 2.98×10^{-2} watt-hr. The specific stored energy that is released by the cell is E′ = 67.7 watt-hr/lb.

This cell should have demonstrated a specific stored energy much closer to the theoretically predicted value of 1,000 watt-hr/lb; but, we tried to recharge the cell and destroyed the graphite electrode in the process. Also, the specific power is low because the melting point of aluminum limits the operating temperature below 1250°F., where the resistivity of the slip is still quite high; 10^5 compared to $10^2 \Omega$-m at 1800°F.

We may conclude that this type cell has limited use unless a separator is found that has a much lower resistivity at 1100°F. Furnace cement (Alkaline Silicates) have a resistivity at this temperature much lower than this ($\sigma \approx 10^4 \Omega$-m).

3.2 High Temperature Dry Cells With 2 Components

A. (Nickel/Slip/Nickel)

This cell was built on a flat ceramic tile around 3" x 3" x 1/2" thick. We drilled 1/4" diameter holes through each of the four corners so that we could mechanically attach wire between pairs of holes on each side and then cement them in for strength and rigidity. We used nickel Chromium wires which is known to resist oxidation up to the temperatures we can reach with our furnaces (2,000°F.). We placed this tile on a hot plate at a temperature of around 300°F. so that the sprays were immediately cured and we sprayed on a layer of nickel paint using a mask to keep paint off of 3 edges including one of the wires. Nickel paint is from Acheson Colloid. It is electrodag # 401. It has a K-sil binder and it is water based. Next, using a mask, we shielded both wires and covered the nickel with a layer of slip. Then, we used the mask again to shield 3 edges and exposed the other wire while we sprayed on a layer of nickel paint. Then, we covered the electrical connections with furnace cement for additional strength. While these materials where curing at room temperature, we applied a voltage and drove current through the cell in an attempt to start inducing a layer of metal in the slip where oxygen has been displaced and pushed across the slip and into the nickel. Some dampness remaining in the cell helped it take the charge. We continued to charge the cell while it cured. Then, we put the cell in the furnace and gradually heated it up to 1800°F. while we continued to charge the cell. This took 10 hours. Finally, we recorded the cell performances as a function of temperature as the cell was heated and cooled from 500°F. to 1800°F. While we were cooling it from 1800°F., we began to notice the deviation from the previous performance. When the cell was cool

enough to inspect, we found that the nickel coating on top had turned to a bright green, it was fully oxidized, and its surface resistivity was extremely high. Fortunately, before this happened, we have very good data on the temperature dependence of open circuit voltage and internal resistance. These are given in Figures 4 and 5. We could not run this cell through many charge-discharge cycles simply because it did not last long enough. We found that the nickel paint turned from gray to bright green and had a very high resistivity due to oxidation of all the nickel. Perhaps, if we had covered the top layer of nickel paint with slip of furnace cement, this might not have happened.

We had built a cell like this before and we used stainless steel wires instead of nickel chromium wires. These wires oxidized in the electrical connections and added a resistance too large for the cell to be effective. This is one of the difficulties of this type of cell. We considered using gold instead of nickel, but did not have the facilities available to make a cell like this.

B. (Nickel Chromium wire/Slip/Nickel Chromium wire)

To avoid the problems mentioned above, we built a cell with nickel chromium wire .015" in diameter wound around an alumina tube 1/8" diameter and 2.5" long. We then fused on a layer of slip .030" thick average, allowing for the grooves along the wire surface. Then, we wound on another layer of wire, and extended the wire from the other end. We also weighed each layer as it was applied and measured its diameter as summarized below:

Weight of the Spindle	1.95g (.129" diameter)
Weight of the Active Nickel Wire	1.13g (.165" diameter)
Weight of the Active Slip	.57g (.195" diameter)
Total Weight of Active Single Cell:	1.70g
Volume of Active Single Cell:	4.24×10^{-2} in^3 = 6.95×10^{-7} m^3
Mean Density of a Single Cell:	2.45×10^3 kg/m^3
Thickness of Wire Layer:	.015"
Thickness of Slip Layer:	.030"
Thickness of a Single Cell:	.045"

Then we coated it with slip and cured it in the air while we were inducing a voltage in the cell by an external power supply. The charge took; so, we gradually heated the cell up to 1800°F. to fuse the slip. The cell had the following history.

History of Nickel Chromium Wire/Slip/Nickel Chromium Wire Cell

Date *	Time	Duration	Temperature	V_{oc}	V_1	R	R_i *	I_c	Remarks
3-23-87		18 hrs	16-1800°F.					.5 - 9.2 MA	Charged at 16 -1800°F. overnite
3-24-87	1000	0	1800	.7	.6	10^3	166.7 Ω		
	1300	3	"	.49	.47	"	42.6 Ω		
	1700	7	"	.44	.42	"	47.6 Ω	67 - 2.1 MA	Charged overnite 14hrs at 25vDC
3-25-87	930	0.5	1750	1.00	.41	"	1.4K Ω		
	1200	3	1850	.87	.83	"	48.2 Ω		
	1700	8	1800	.59	.56	"	53.6 Ω	66 - 5.2 MA	Charged overnite 14hrs at 25vDC
3-26-87	900	0	"	.87	.43	"	1.02KΩ		
	1200	3	1850	.63	.58	"	86.2 Ω		
	1700	8	1800	.36	.33	"	90.9 Ω	65 - 6.8 MA	Charged overnite 14hrs at 25vDC
3-27-88	900	0	"	.60	.25	"	1.4K Ω		
	1200	3	1825	.31	.26	"	192.3 Ω		
	1600	7	1800	.22	.19	"	160.0 Ω	65 - 7.21 MA	Charged over weekend 62hrs at 25vDC
3-30-87	1030	0	1850	.54	.41	"	320.0 Ω		
	1330	3	"	.29	.26	"	120.0 Ω		
	1730	7	"	.18	.17	"	60.0 Ω	66 - 8.5 MA	Charged overnite 14hrs at 25vDC
3-31-87	900	0	1750	.37	.11	"	2.36KΩ		
	1200	3	1850	.25	.23	"	90.0 Ω		
	1500	3	1900	.058	.055	"	50.0 Ω		

Typical Performance Characteristics at 1800°F. are:

Open circuit voltage	.65
Loaded voltage	.62
Load resistance	1000 Ω
Internal resistance	80.6
Power	4.77×10^{-3}
Weight of active ingredients	1.70g
Specific Power	1.27 watts/lb

The resistivity $\Delta = R_i A/S_o = 80.6 \times 2.5 \times \pi \times .180 \times .0254/.030 = 90.6\Omega - m$. This is the resistivity at 1800°F.

Although the specific power for this prototype cell is rather low, 1.27 watts/lb, we were forced to use exceptionally thick layers of Nickel Chromium wire (.015"), and slip (.030"); however, Nickel Chromium wire is available at one-tenth of this thickness (.0015"), and slip layers can also be reduced by a factor of 10 or more (.003" or less). The result, according to equation 9, would be an increase in specific power by a factor of 100, or 127 watts/lb. Referring to figure 6 for specific power versus specific stored energy, we see this to be superior to that of the most advanced cells.

We discharged this prototype for 12 hours at 1.27 watts/lb, or 10.2 watt-hrs/lb. Obviously, we could have continued the discharge for many more hours if desired.

An unexpected and unexplained observation is that the internal resistance of the cell at a fixed temperature decreases typically from around 300Ω to around 60Ω over the first few hours of its discharge, and during the first few hours of recharge its resistance increases a similar amount! Perhaps, while charging, we are displacing oxygen from the slip into the Nickel Chromium, and perhaps, the resistivity of Nickel Chromium Oxide is greater than that of slip. During discharge, oxygen is displaced from the Nickel Chromium oxide back into the slip, and resistance may decrease. This is just speculation, but it seems reasonable.

We built a similar cell, but with furnace cement (Alkaline Silicates) replacing the slip. Performance was similar, except that we reached R_i approximately 100Ω at 1400°F. instead of 1800°F. Hence, we conclude that furnace cement has a lower resistivity than slip; however, it seems that some material evaporates from the furnace cement, and it gradually becomes transparent and the induced voltage decreases. Perhaps, sodium and potassium in the induced electrode evaporates. There may be a lower temperature at which furnace cement could be useful as a stable separator.

3.3 Low Temperature Damp Cells With 3 Components

A. $^{+}$(Graphite/Magnesium Oxide/Aluminum)$^{-}$

This cell was built between glass slides 1" x 3" long. Construction technique was similar to that used in category 1 (High Temperature Dry Cells With 3 Components), except that the separator was applied by electrogasdynamically coating MgO powder on both slides, to a thickness slightly less than 1 mil, then carefully placing these two halfs together. Attaching and cementing the wires near their ends, they were mounted inside a plastic container with a wet paper towel to maintain humidity. A computer recorded the voltage across a load resistance as a function of time. The main result is that voltage always decreased during the discharge, reaching an unacceptably low level after only a few hours. The voltage could be restored by recharging the cell, but the decrease would repeat itself. This is shown in the computer printout, Figure 9.

B. $^{+}$(Graphite/Aluminum Oxide/Aluminum)$^{-}$

This cell was identical to the one above except that aluminum oxide powder was deposited instead of magnesium oxide. The test results were essentially the same except that this cell lost voltage during discharge even faster than the magnesium oxide cell. Results are given in Figure 10. A possible explanation is that the powder gets slightly wet and metal ions are moving towards the graphite. These ions after losing their charge to the graphite, coat the graphite and begin to change its surface towards that of the coating metal. This, of course, would reduce the voltage. Recharging removes these ions and restores the voltage. It is possible that the aluminum is less reactive with water and will not go back into solution, and come off the surface as readily as magnesium will. This idea is given more credibility when we use sodium chloride in the separator, because the sodium ions are more reactive with water and air, so they do not remain on the graphite, and the voltage does not sag.

C. $^{+}$(Graphite/Sodium Chloride in Paper/Aluminum)$^{-}$

This cell was constructed similar to those above, but a piece of hair wave paper approximately 1 mil thick serves as the separator. After building the cell, a small voltage was observed, but with very large resistance, like $10^{5}\Omega$, then by adding several drops of concentrated sodium chloride approximately 0.6 volt was obtained, and the resistance dropped to approximately 1,000Ω. After 4 days, we saw through the glass that a small section of the aluminum was beginning to disappear. We tried to bring the aluminum back by recharging, but without success. The characteristic performance before stopping the test were:

$V_o \approx .6$
$V \approx .41$
$R \approx 1000$
$R_i \approx 463\Omega$
$P \approx 3.63 \times 10^{-4}$ watts

The weight of the active ingredients in this cell is $\approx 10^{-4}$ kg, so the specific power is $P' \approx 3.63$ watts/kg = 1.65 watts/lb. The cell ran for approximately 4 days or 100 hours before we started noticing missing aluminum, so the specific stored energy was $E' = 167$ watt-hrs/lb, and the specific stored charge $Q' \approx E'/V = 407$ ampere-hrs/lb. Although the specific power is small compared to conventional primary cells, the specific stored energy and specific stored charge are larger. Furthermore, the cost of materials and the cost of fabrication of wound cells of these materials would be much less.

D. $^{+}$(Graphite/Sodium Chloride in Paper/Aluminum)$^{-}$ (wound)

This cell has a strip of aluminum and a strip of graphite coated paper separated by 2 strips of paper all wound on a spindle approximately 1/2" in diameter with the active area of the cell approximately 2" x 10". The edges of the aluminum on one side and graphite on the other side are connected by graphite paint to wires. During test, the cell was suspended in a plastic container with a wet sponge secured to the top of the container. The container was heated from the bottom by placing on a warm surface and this way we avoided condensation forming on the cell. A thermometer was installed in the container and the following data was collected.

$^{+}$(Graphite/Sodium Chloride in Paper/Aluminum)$^{-}$
Rolled Cell #312
The cell was kept under a 1000Ω load.

Time	Temperature	V_{oc}	V_l	R_l	R_i
1100	40°C.	.75	.67	10^3	119 Ω
1200	50	.66	.57	"	157 Ω
1300	60	.74	.65	"	138 Ω
1400	70	.71	.66	"	75.8Ω
1500	80	.67	.60	"	116.7Ω
1600	90	.67	.62	"	80.6Ω
1700	100	.58	.53	"	94 Ω

Discharge was started on 3-13-87. The cell was placed in a container with a small amount of humidity. A 1,000Ω load was put on the cell. At room temperature the cell has an average V_o of .57, V of .47 and 212 Ω internal resistance. As of the date of this writing it has been discharging for 42 days. The average temperature has been 26°C.

It should be noted that when the container was placed in a pan of water, and the water was heated up to boiling, the container was heated as high as 100°C. The open circuit voltage increased steadily as the temperature rose, but the internal resistance did not steadily decrease. It seems to vary slightly, but unpredictably. It is difficult to repeat this experiment because there are so many variables, and the container was leaking so there is pressure variation, temperature variation, dampness variation; nevertheless, at the best operating point T = 80°C., the open circuit voltage was .708, the loaded voltage was .560, the load resistance 1,000 Ω, the internal resistance was 264 Ω, the power was 1.19×10^{-3} watts, weight of the active components

in the cell was approximately 11×10^{-4} kg; therefore, the specific power was approximately 1.08 watts/kg. = .492 watt/lb.

This cell was left discharging at approximately room temperature with R/R_i = 1,000Ω/306Ω for 40 days. (At the writing of this report, this cell was still discharging.) The voltage remained fairly constant over this period and the power output was steady at $P \approx V^2/R \approx 1.04 \times 10^{-3}$ watts, and the energy extracted was $E = P\,T \approx 1.00$ watt-hr. The specific power and the specific energy was $P' \approx .945$ watt/kg = .430 watts/lb, and $E' \approx 910$ watt-hr/kg = 414 watt-hrs/lb. The theoretically predicted value from section 2.7 was approximately 1,000 watt-hr/lb, which the cell might achieve as it continues to discharge. It has already exceeded the specific stored energy of most commercial batteries.

It should be noted that the power density of cell C < cell B. This is due to the increased distance from the wire on the positive terminal to the active part of the cell. There is an unusually high resistance along the graphite coated paper causing both cells to have additional internal resistance. This problem is discussed in greater detail in Section 4.

E. $^{+}$(Graphite Coated Aluminum/Sodium Chloride in Paper/Aluminum)$^{-}$ (Wound)

This cell is the same as Cell D, except that the graphite coated paper was replaced by graphite coated aluminum in order to reduce the resistance along the positive electrode. The results were V_o= .66v, V= .60v across R= 10^2 ohms, so R_i= 10 ohms, compared to R_i= 264 ohms for cell D. The weight of the cell was w= 2.42×10^{-3} lb., and the volume was v=6.6×10^{-2} in^3; so, its specific power was P"=9.27 watts/lb.,and its power density was 4.32×10^4 watts/m^3. Its specific stored energy was 500 watts-hr/lb. at maximum power. Also, the cost of the cell was primarily due to the cost of aluminum foil which is $8.00/lb. retail price.

Unfortunately, the resistance of the cell gradually increased as the aluminum under the graphite coating gradually oxidized, because there were pinholes in the coating through which humid air could attack the aluminum which is part of a short-circuited $^{+}$(Graphite/Aluminum oxide/Aluminum)$^{-}$ cell.

In the future, we will get essentially the same performance by replacing the graphite coated aluminum with copper .0007" thick which is now commercially available at $28.00/lb. Since the copper is reusable, the actual cost of this type primary cell can be reduced considerably. Although we learned of the commercial availability of this thin form of copper too late in the program to build a cell, we have had enough experience with copper in other cells to estimate the performance and cost of such a cell, and this is shown in Table 2.

3.4 Low Temperature Damp Cells With 2 Components

A. (Graphite Coated Paper/Sodium Hydroxide in Paper/Graphite Coated Paper) (wound)

The cell consists of 2 sheets of graphite coated paper 11" long and 3" wide and 2 uncoated paper sheets 11" long and 4" wide, and wound on a spindle approximately 1/4" in diameter, the edges are displaced so wires can be attached to the ends. After winding, the cell is soaked again in concentrated sodium hydroxide and dried and soaked again in concentrated sodium hydroxide and then it is charged with a 24 volt power supply until it dries out and creates an electrode of sodium. The charging is continued in a humid container for 48 hours. The performance was dissappointing because V_o never exceeded .3 volt, as if the induced negative electrode was discontinuous. Furthermore, we could not take this cell through many charge-discharge cycles because after operating at elevated temperatures in a humid environment the sodium hydroxide embrittled the graphite coated paper, and the cell began to crumble.

B. (Graphite Coated Paper/Sodium Chloride in Paper/Graphite Coated Paper) (wound)

To avoid embrittlement by sodium hydroxide, we rebuilt the cell and used sodium chloride instead. Unfortunately, we were never successful in developing more than .03 volt open-circuit, despite long periods of charging. We suspect that the cell remained wet at various locations despite vain attempts to dry out the cell and humidify it uniformly. These localized wet spots partially short-circuit the cell and prevent it from growing a uniform layer of sodium as the third component, or negative electrode.

C. (Copper/Furnace Cement in Paper/Copper)

This cell consisted of 2 sheets of copper 1" x 3" separated by Ecusta hair wave paper saturated with wet furnace cement (Alkaline Silicates). After drying the cell until slightly damp, and charging with 24 volts for 4 hours, $V_o = 1.00$ volt and $R_i = 100$ ohms. Although we used thick copper electrodes, copper sheet is available at .0007" thickness, and such a cell would have a total thickness of .002", volume 6×10^{-3} "^{3} and weight 1.95×10^{-3} lb. The maximum power output is $P = 2.5 \times 10^{-3}$ watt; so, the specific power is $P' = 1.28$ watts/lb, and a power density of 2.54×10^4 watts/m^3. Again, the theoretical specific energy at maxium power is $E' \approx 500$ watt-hr/lb. With Phase I coming to an end, we could not determine the number of possible charge-discharge cycles, but experience suggests a large number.

3.5 Batteries of Cells

A. In Parallel

In each of the four categories we were successful in stacking cells in parallel; i.e. a thin layer of the positive electrode material, then a thin layer of separator material. It covers all except the left edge of the positive electrode material, then a thin layer of negative electrode material that extends beyond the right edge of the separator material, then a layer of separator material, then a layer of the positive electrode material, etc. Then, all of the exposed edges on the left side of the stack are joined by a conductive paint to form the positive terminal while all of the exposed edges on the right side are joined by conductive paint to form the negative terminal as shown in Figure 2. Of course, in case of 2 component cells in which the negative and positive electrode material are the same, this stack has to be charged to form layers of metal on the negative electrodes. This technique has proven effective in all categories as long as the materials and methods of fabrication are compatible with the environment.

Towards the end of the Phase I research, we learned that the parallel stacked cells like that shown in Figure 1, with Graphite coated paper instead of Graphite coated Aluminum, has an inherent defect that causes a large internal resistance thereby limiting specific power. To get from the positive terminal to the negative terminal through the cell, the current must flow full length L of the electrode, through their very narrow cross sectional area, $S_+ W$, where W is the width of the cell, which introduces a resistance $R' = \delta' L/S_+W$. In series with what we have been assuming is the internal resistance of the cell; i.e. the resistance of the separator $R_o = \delta S_o/LW$. The ratio of the two resistances is therefore

$$R'/R_o = (\delta'/\delta)(L^2/S_o S_+).$$

In the glass slide cell we built, and the wound cells we have been building $L^2/S_o S_+ \approx 2.5^2/.001^2 \approx 6.25 \times 10^6$. Thus, the only time we can justify neglecting R′ compared to R is when $\delta'/\delta \leq 10^{-7}$. If the paper separator is very wet with salt water, $\delta \approx 1\Omega m$. The resistivity of Aluminum is $\delta' = 10^{-7}$ ohm-m. However, the resistivity of the grahite coated paper we have been using is much higher, around $10^{-2}\Omega$-m. Hence, it is now apparent that internal resistance of the cells in category 3 and 4 is primarily due to the resistance in the graphite coated paper. Acheson Colloid claims to have a conductive graphite paper with some silver in it that has a much lower resistivity, and might greatly alleviate this problem.

To check on this analysis, we directly measured the resistance across 2 1/2" of graphite coated paper 1" wide and 1 mil thick to get $R' = 400\ \Omega$; then, we measured the resistance across a

piece of paper damp with concentrated salt water, 1" X 3" and 1 mil thick, sandwiched between 2 pieces of aluminum foil, and got $R_o = 5\ \Omega$. Thus, $R'/R_o \approx 80$.

In category 2, cell A developed this problem because the nickel electrode oxidized and developed a very high resistivity. We avoided this problem when cell 2B by using nichrome wire that did not oxidize, and using a value of S_o and S_+ ten times thicker than usual.

The cell in category 1 probably did not have this problem because it was operated only at 1100°F. where the separator still had a very high resistivity.

Cell C in category 3, low temperature damp cell with 3 components, showed the aluminum foil oxidizing along the edge closer to the positive terminal of the cell as if electrons would rather not travel full length of the high resistance graphite coated paper, but it jumped across the separator to the edge of the aluminum. The aluminum in the wound cell may also be consumed in this fashion, but there is no way to observe this. While in the discharge mode, the electrons would prefer to run down the aluminum to this edge and then jump across close to the positive terminal on the graphite; however, we did not observe reduction of aluminum oxide even in the long periods of charging. When we did build a cell with copper foil replacing the graphite coated paper, the aluminum was consumed more uniformly. A random array of pin holes appeared, the number increased until they coalesced and the aluminum disappeared. Recently, Copper .0007" thick has been available by Somers Corp. of Waltham, Mass. Unfortunately, it costs $28.00/lb, but this may prove to be acceptable in high performance cells, especially if the copper is not consumed. Another chance for improvement seems to be the graphite coated paper of much lower resistivity, which Acheson Colloid thinks it can provide at reasonable cost. Still another solution is the one shown in Figure 1 in which the positive electrode is graphite coated aluminum foil which is more expensive than paper possibly, but it will avoid this problem. However, another problem is introduced if any of the aluminum is exposed, because it is part of a short circuited cell $^{+}$(graphite/aluminum oxide/aluminum)$^{-}$. Exposed aluminum will surely be oxidized and oxidation may continue gradually and consume much of the aluminum, especially if the environment is humid.

B. In Series

To avoid the problem of running current lengthwise through relatively high resistivity graphite and binder, we built a battery consisting of series stacked cells, that were made of 3" X 3" square of 1 mil thick aluminum foil, painted on one side with graphite paint, and separated by 1 mil thick Ecusta hair wave set paper having the same cross section and soaked with saturated sodium chloride in water. After drying this stack of 8 panels slowly in an oven at 200°F. with a

lightweight on it, the edges were sealed with silicone sealant and wires were attached to each end. In a humid environment, the battery absorbs water vapor and air molecules but does not pass liquid. Unfortunately, after two attempts, we failed to satisfactorily insulate the edges of the cells from one another. Special attention will have to be given to this problem. The solution will probably require that the edges of each panel must be coated with thin films of insulation.

Although it is tedious to build large batteries this way without automation, with it, it is feasible to make 24 volts or 100 volts DC batteries that are approximately .048" and .2" thick, respectively. This could be made as much as 1 m^2 in area and to be a structural part of the walls in homes or vehicles, etc.

In the category, low temperature damp cells with 2 components, we tried in vain to produce a battery consisting of alternative layers of graphite coated paper and paper. After charging, we induced an EMF equal to that of a single cell, regardless of the number of layers in a stack! Apparently, the oxygen ions can find their way through the intermediate layers of graphite as if they were not there. This does not occur in the 3 component stacks because the aluminum foil prevents the oxygen ions from moving through. Graphite coated paper will probably take the electron from the oxygen ion, but it still lets oxygen diffuse right through its pores. On the other side, where we are trying to induce a layer of metal, the oxygen that diffuses through simply reoxidizes that metal. The only place where an electrode is induced on the surface of the graphite is at the bottom of the stack where electrons are pushed in without oxygen by the external power supply. Hence, we get in effect, just a single cell.

Replacing the graphite layer with copper foil avoids this problem, and allows the voltage to multiply, but copper is so heavy and expensive that this maybe an impractical approach. In any event, these stacked cells require too much handling and it is easier to make wound cells, and stack them end to end to get any desired voltage.

3.6 Large Wound Cells

We built a large version of the wound cells described under the category, low temperature damp cells with 3 components. The machine shown in Figure 11 under category 3, was capable of simultaneously winding a strip of aluminum and a strip of graphite coated paper from Ecusta with 2 strips of Ecusta paper insulating them. The resulting cell on a 1" spindle has an outside diameter of 5", and a total length of 265 ft, or 1.27×10^4"^{2} total active area. The ends of this coil where painted with radial spokes of conductive paint and tied to the spindle to form the opposite poles of the cell. The cell was soaked in concentrated sodium chloride, then dried before installing it in a humid enclosure. The performance characteristics of this cell are:

V_o = .720 volts
I_s = .75 amp
$R_i = V_o/I_s$ = .96 Ω
R = .96 Ω
P = .135 watts.

The volume of the cell is $3.98 \times 10^{-4} m^3$, so its power density is 340 watts/m^3, the weight of the cell is 2.36 lb, so its specific power is $P' = 5.71 \times 10^{-2}$ watts/lb. The temperture in the enclosure is 78°F. The contract will be over before we can fully discharge this cell and oxidize all the aluminum in it. But the theoretically predicted stored energy is $E' \approx 500$ watt-hr/lb, at maximum power so with 2.36 lbs, we expect 8.94×10^{-3} hours, or 372 days, of discharge at .135 watts, which is superior to most storage cells. Certainly, this type cell in mass production would be much cheaper. Of course, if the resistivity of the graphite paper can be reduced, specific power can be increased substantially.

APPENDIX I

OPERATING CHARACTERISTICS OF THERMOVOLTAIC CELLS

Operating characteristics of these thermovoltaic cells and batteries can be described as follows:

A. OPEN CIRCUIT VOLTAGE V_o
The first and second laws of thermodynamics can be used to predict that the open circuit voltage of such a cell is,

$$V_o = V^* + T(dV_o/dT) = V^* + T \qquad (1)$$

This is the Gibbs-Helmholtz relationship, and it is verified experimentally by the plot of V_o vs. T in Figure III, which is a straight line.

B. SHORT CIRCUIT CURRENT I_s
When the cell is shorted by a wire, the current that flows is limited only by the internal resistance R_I, i.e.,

$$I_s = V_o/R_I \qquad (2)$$

Plots of V vs. I are always found to be straight lines, indicating that $V = V_o - I\ R_I$. This is because current densities are low and are not limited by the rate of chemical reactions.

C. INTERNAL RESISTANCE R_I If the thickness of the separator is S, its area A, and its resistivity δ, then,

$$R_I = \delta\ S/A \qquad (3)$$

Using the solid state physics model in which the semiconductor has electrons in its conduction band that attach to oxygen atoms to form oxygen ions and leave positive holes in the lattice, it is predicted that the resistivity would depend upon temperature according to the relationship,

$$\delta = \delta^* \exp(a/T) \qquad (4)$$

This has been verified by measuring R_I at various temperatures and plotting log R_I vs. 1/T to get a straight line as shown in Figure 3. Note that R_I decreases several orders of magnitude as temperature increases from room temperature to 1200°F.

D. SPECIFIC POWER P′

With an external resistance equal to the internal resistance, maximum power is drawn from the cell or battery, and if the power is P, and the mean density of the materials is $\bar{\rho}$; then, power/mass =,

$$P' = \frac{P}{\bar{\rho}AS'} = \frac{V_o^2}{4\rho R_I AS'} = \frac{V_o^2}{(4\rho\ S^2(S + S_+ + S_- + S^*)/S)} \qquad (5)$$

Where S_+ and S_- are the thickness of the plus and minus electrodes and S^* is the thickness of the structure.

Based on experiments to date, and using commercially available material with improved methods of construction, we can expect to achieve at 1200° F. operating temperature,

V_o = 2 volts

$\bar{\rho} = 2\times10^3$ kg/m^3

$\sigma = 10^4$ ohms-m

$S = 10^{-5}$ m

$(S_+ + S_- + S^*)/S = 1$

Therefore, a specific power of P = 253 watts/kg = 114 watts/lb. This assumes that we use commercially available .0004" aluminum foil coated with an oxide .0002", which can be applied with commercially available electrogasdynamic (EGD) spray equipment. It would be difficult to increase the specific power much beyond this value with this fabrication technique; however, it is competitive with other advanced batteries now in development (Figure 1). Other methods of fabrication such as vacuum deposition would result in much higher specific powers, but coating rates are so slow that the batteries would be extremely expensive.

We used an experimentally determined value for resistivity of the oxide coating, and there is reason to believe with further research this value can be reduced considerably. Our oxide coating material is proprietary and we already know certain additives decrease its resistivity. Also, certain heat treatments reduce its resistivity. Many researchers are working on improving the conductivity of solid state ionic conductors, and we expect that some of these findings will be applicable to this problem (Ref. 2).

E. SPECIFIC ENERGY E′

The specific energy of the cell may be written as follows; stored electrical energy/mass = (6)

$$E' = \frac{V_o(g)}{m_o} \times \frac{\text{mol. wt. O}}{2/3 \times \text{mol. wt. Al}} \times \frac{(PS)Al}{}$$

$$(\rho S)_{Al} + (\rho S)_{Al_2O_3} + (\rho S)_C + (\rho S)_*$$

where q/m is the charge to mass ratio of oxygen and ρS is the product of density and thickness of the materials indicated by the subscripts.

In particular example, energy/mass =

$$(2) \times (10^8/3) \times (16/((2/3) \times 27)) \times (1/1) + 1 + .5 + 0 =$$
$$8.89 \times 10^6 \text{ joules/kg} =$$
$$2.47 \times 10^3 \text{ watt-hr/kg}$$
$$1.12 \times 10^3 \text{ watt-hr/lb}$$

This is about five times larger than that predicted for advanced batteries now under development, and this is because there is almost no additional weight devoted to structural members in and around the batteries.

F. CHARGE-DISCHARGE CYCLES

The time required to fully discharge a cell is t = 1120 watt-hr/114 watts = 10 hours. During this time, the internal resistance of the cell would increase by approximately a factor of 2, because the thickness of the oxide layer would be doubled as the aluminum oxidizes. However, the cell can be recharged and its internal resistance lowered as the record of V_o and R_I at 900^0 F. shows while the cell is discharged and charged several times (Figure 4).

G. THERMAL CHARACTERISTICS

When the external resistance equals the internal resistance of a battery it delivers maximum power/volume, but its efficiency is only 50%, i.e., half of the chemical energy released is delivered as electricity and the other half is delivered as heat within the battery. Because the heating effect is proportional to the volume and the cooling effect is proportional to the area of the battery, the thickness of insulation required to maintain the operating temperature decreases as the size of the battery increases. To be precise, let the surface area of the battery be A′ and the thickness of the insulation be S′, and its thermal conductivity K. Then, the thermal power that must be conducted through the insulation is,

$$Q = P = A'K(T-T_o)/S' \qquad (7)$$

where T_o is the ambient air temperature.

Now, introducing the power density P/V, and a mean battery size defined by $\bar{S} = V/A'$; then, it can be shown that,

$$\bar{S}S' = K(T-T_o)/(P/V) \qquad (8)$$

Assume, for example, that this battery is enclosed in quartz fiber insulation having K = .0866 watts-m/m^2-^{0}C, and $T - T_o$ = 600 ^{0}C. amd P/V = 250 watts/kg x 2 x 10^3 kg/m^3 = 5 x 10^5 watts/m^3; therefore, $\bar{S}S'$ = 1.04 x 10^{-4} m^2 When S′ = $\bar{S}$, the volume of insulation = volume of the battery, and adding the

insulation cuts the specific power and specific energy in half. For cubically shaped batteries having the size of length X, volume X^3 and area $5x^2$; $S = X/6$. Therefore, $SS' = (X/6)^2 = 1.04 \times 10^{-4} m^2$, and $X = 6 \times 10^{-2} m$. A battery of this size would have power output of $P = 5 \times 10^5$ watts/$m^3 \times 2.16 \times 10^{-4}$ m^3 = 108 watts. In a battery larger than this size the weight of the insulation would be less than that of the battery, and by the time we reach sizes larger than 1,000 watts the weight of the insulation would be negligible. In fact, for batteries of 1,000 watts of more it would probably be necessary to provide special cooling to prevent the battery from over heating.

Thermal enclosures for modern high temperature batteries have been built and investigated by several researchers (Ref. 3). Because the thermovoltatic battery described here is so simple in construction, and electrical connections to it are also simple, providing it with a thermal enclosure is relatively straight forward.

The thermodynamics of these batteries, once understood, can provide some special benefits, e.g., the battery can be made to heat itself by decreasing the external resistance so that most of the chemical energy is deposited in the battery as heat. Also, when the load resistance is larger compared to the internal resistance, the battery can cool itself and convert some of its thermal energy directly into electricity, because the open circuit voltage consists of two parts; that due to chemical energy released plus that due to heat extracted from the battery environments; i.e.,

$$V_o = V^* + T(dV_o/dT) = V_o + \beta T \qquad (9)$$

The second term is identified with entropy changes. Referring to Figure 2 this cell has $d V_o/dT = 7.6 \times 10^{-4}$ v/°K and V_o = .12 v; therefore, at T = 1200 °F. = 922 °K, $T(dV_o/dT)$ = .701 V. Thus, the cooling effect is an appreciable portion of the total voltage; i.e.,

$$.701/(.701 + .12) = 853 \qquad (10)$$

In conclusion, the thermovoltaic battery is an attractive alternative to conventional liquid electrolyte batteries and advanced high temperature batteries now under development, because they have the potential to achieve much higher specific energy and power. Other advantages are their simplicity of construction, safety, reliability, and ability to rapidly charged and discharged without deterioration. The latter is possible because there are no secondary reactions in these batteries and the current density, or current per unit area is so small that there are less physical changes to the electrode surfaces than in conventional batteries.

The thermovoltaic battery relies on having a very large surface area rather than very large current density.

APPENDIX II

SPECIFIC POWER VS. SPECIFIC STORED ENERGY

Consider a thermovoltaic cell of total thickness $L = S_+ + S_- + S$, where S_+ is the thickness of the positive electrode, and S_- is the thickness of the negative electrode and S is the thickness of the oxide separator between them. Note that the thickness of the positive electrode remains constant as does the overall thickness; hence, during discharge as the thickness of the negative electrode decreases due to oxidation, the thickness of the oxide separator increases by an equal amount, and vice-versa during charge.

If the area of the cell is A, and its resistivity is , then, its internal resistance is $R_i = S/A$.

Also, let the external resistance be R, through which a current I flows generating a voltage $V = IR$ and delivers electrical power,

$$P = I\,V = I^2R = V^2/R \qquad (1)$$

Also, if the open circuit voltage is V_o, then the current is,

$$I = V_o/(R + R_i) \qquad (2)$$

The specific stored energy of the cell is the chemical energy stored in the cell per unit mass of the cell less that which would be converted into heat as current passes through the internal resistance of the cell, i.e.,

$$E' = V_o(q/m)_O \cdot \frac{\text{mol. wt. O}}{2/3\ \text{mol. wt. Al}} \cdot \frac{\rho_- S_-}{\rho_- S_- + \rho_+ S_+ + \rho S - (R_i/R)E'} \qquad (3)$$

Now, introducing the mean density $\bar{\rho} = (\rho_- S_- + \rho_+ S)/L$, and for simplicity, assume that $\rho_-/\bar{\rho} \approx 1$, then,

$$\frac{E'}{E_o} = \frac{R/R_i}{R/R_i + 1}\left(1 - \frac{S_+}{L} - \frac{S}{L}\right) \qquad (4)$$

where,

$$E_o = V_o(q/m)_O \times \frac{\text{mol. wt. O}}{\text{mol. wt. Al}} \qquad (5)$$

Obviously, this analysis can be generalized to include oxidants other than aluminum, and oxidizers other than oxygen; but, the result shows that for any given cell, the specific stored electrical energy depends on two parameters, S/L and R/R_i, which indirectly also depends upon S/L.

It can be shown using eqs. 1, 2, and 3 that specific stored

power is also related to these two parameters; i.e.,

$$P'/P_o = 4 \times \frac{R/R_i \times L/S}{(R/R_i + 1)^2} \times \frac{L}{S} \qquad (6)$$

where,

$$P'_o = V_o^2/4\bar{\rho}\sigma L^2 \qquad (7)$$

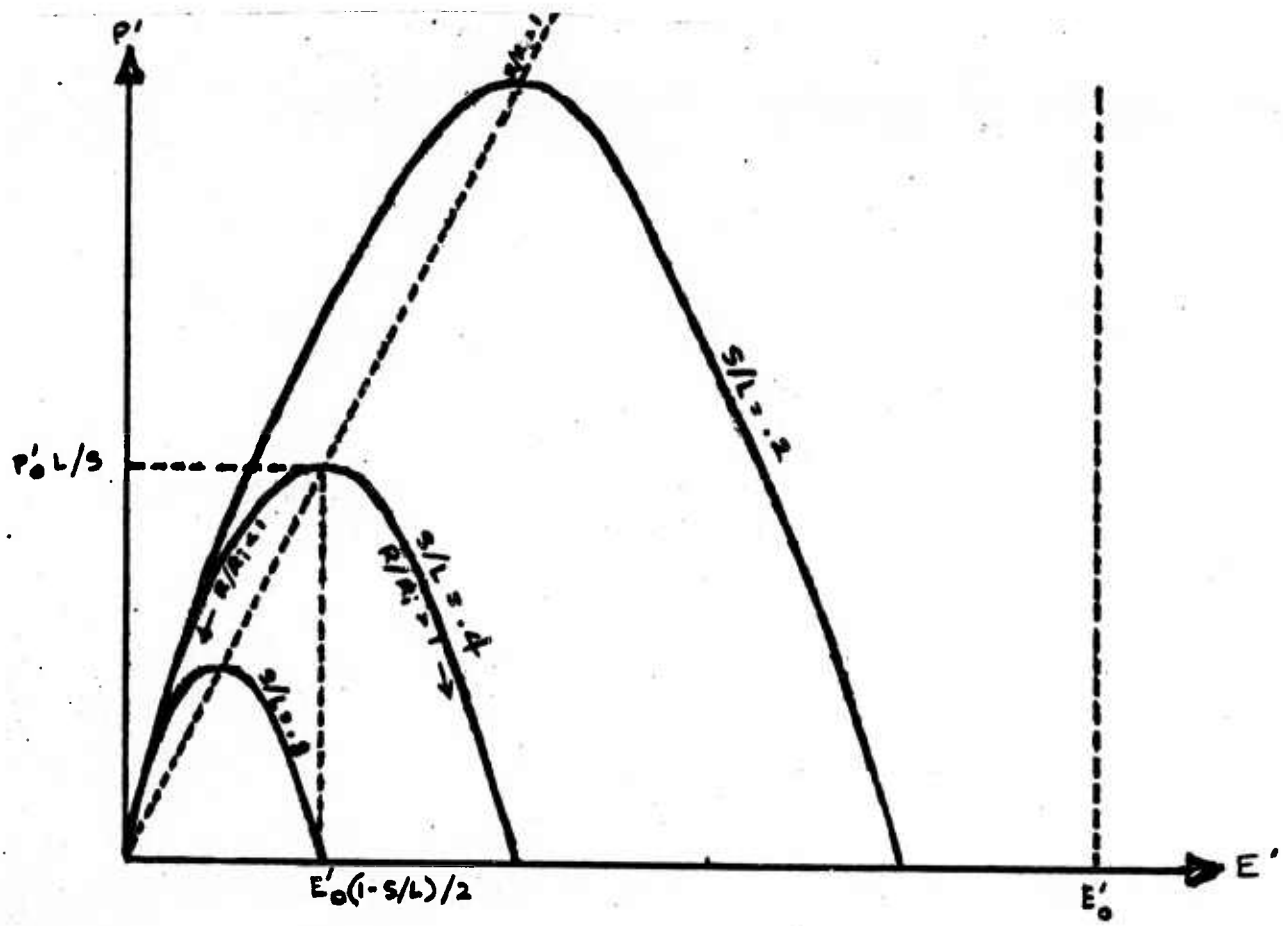
We can eliminate R/R_i from relationship between E' and P' with some algebraic manipulating, and the result is,

$$P'' = E''(1-E'') \qquad (8)$$

where, $P'' = P'/P_o(L/S)$ (9)

$$E'' = E'_o/(E_o(1 - S_+/L - S/L)) \qquad (10)$$

The plot below shows qualitatively how P' and E' are related, and how this relationship depends on the parameter S/L, or the fraction of the cell that is discharged. In this plot, we assume that S_+/L is much less than 1, which is generally the case.



It should be noted that as the parameter S/L increases (cell discharging) the parabolas becomes smaller and shifts to the left. For any given value of S/L, tha peak of the parabola corresponds to $R/R_i = 1$; and, $R/R_i > 1$ is to the right of the peak.

To determine the relationship between discharge time t and relative increase in thickness of the oxide layer, S/L, or the relative decrease in the thickness of the negative electrode, jS_-/L, consider the following relationship between specific power and the rate of decrease of specific stored energy; i.e.,

$$P' = - dE'/dt$$

Then, introducing the characteristic discharge time $t_o = E'_o/P'_o$ and, using eqs. 4 and 6,

$$4\ L/S)/(R/R_i + 1) = - d(1 - S/L)/d(t/t_o) \qquad (11)$$

After integrating and introducing the initial condition,

$t\ (0) = 0$ and $S(0) = S_o$, we get,

$$t/t_o = (R/R_i + 1)((S/L)^2 - (S_o/L)^2)/8 \qquad (12)$$

Now, consider a typical case in which,

$E'_o = V_o(q/m)_{l.c.} \times 0$ m.w./(2/3) Al m.w. $= 2(10^8/8)(16/18)$ $= 2.22 \times 10^7$ joules/kg $= 7.66 \times 10^3$ watt-hr/kg $= 2.80 \times 10^3$ watt-hr/lb and, $P'_o = V_o^2/4\bar{\rho}\delta L^2 = (2^2/4) \times 2 \times 10^3 \times 4 \times 10^4\ (25 \times 10^{-6})^2 = 20$ watt/kg $= 9.09$ watt/lb.

Also, the characteristic discharge time is $t_o = E'_o/P'_o = 308$ hrs.

Plus, to fully discharge a cell, that was initially fully charged ($S/L \approx 0$), with $R/R_i \approx 1$, the discharge time will be $t = t_o/4 = 77$ hours. However, near the end of the discharged as $S/L \approx 1$, specific power is very low. The trick is to operate these cells close to their fully charged condition, where specific power and specific stored energy are still high. For example, consider operating with S/L increasing from .1 to .4, which is equivalent to S_-/L decreasing from .9 to .6; then, the discharge period is $t = t_o(.4^2 - .1^2)/4 = 308\ (.15)/4 =$ $=11.55$ hours. Hence, according to the plot in Figure 1 from Ref. 1, recharging such a cell daily would keep it operating in a range suitable for electric vehicle, i.e., $25 \leq P' \leq 100$ watt/lb.

In order to achieve even higher power density, the best procedure is to decrease the overall thickness of the cell by a factor of .32. This would increase this range by a factor of 10 which would be far superior than any modern batteries as shown in Figure 1. Furthermore, it should be noted that to decrease L = 1 mil to L = .3 mil is well within the capability of current technology; so, this is a reasonable next step.

It should be noted that if the external resistance is adjusted so that $R/R_i = 1$, then the discharge is always at maximum specific power (dash lines in Figure G) and the conversion efficiency is 50%; i.e., half of the chemical energy released is converted into heat. The efficiency is higher if $R/R_i > 1$; e.g., constant specific power (solid lines in Figure G).

APPENDIX III

CONVERSION EFFICIENCY OF THERMOVOLTAIC CELLS

Consider a cell that is charged at temperature T_c with current I_c for a period of time t_c, at voltage V_c and having an internal resistance R_i (T_c)

Also, consider the same cell being discharged at temperature T with current I for a period of time t, at voltage V and with internal resistance $R_i(T)$

Assuming that there are no mechanisms for losing charge stored in the cell, then $I_c\ t_c = I\ t$, and the efficiency of the cell is

$$\eta = \frac{\text{electrical energy output during discharge}}{\text{electrical energy input during charge}}$$

$$= V/V_c = (V^* + \beta T - I R_i (T)) / (V^* + \beta T_c + I_c R_i (T_c)) \qquad (1)$$

If the discharging and charging are done and the same temperature $(T = T_c)$, then the only way to increase the conversion efficiency is to reduce joule-heating during both processes, i.e., reduce $I R_i$ and $I_c R_i$.

This suggests that the charging process and discharging process should be as slow as practical.

When the temperature coefficient β is reasonably large, there is another interesting way of increasing the energy conversion efficiency of thermo-voltaic cells, i.e. charge at a low temperature and discharge at a high temperature $(T_c << T)$.

However, it should be remembered that generally $R_i (T_c) >> R_i (T)$, so it would be necessary to have $I_c << I$.

Fortunately, there is a way around this restriction. Near room temperature, it is possible to reduce the internal resistance of the cell by exposing it to a humid environment, and then $R_i (Tt_c) <$ or $= R_i (T)$.

This simplified analysis neglects the initial part of the charge and the final part of the discharge where the cell voltage varies with time because the interim period is much longer than these transient periods.

Noting that during charging, the open circuit voltage is $V_o = V^* + \beta T$ and the current is $I = V_o / (R + R_i)$ where R is the external resistance, and also noting that the charging voltage is $V_c (T_c) = V_o (T_c) + I_c R_i (T_c)$; then, the energy conversion efficiency may be written in the form

$$\eta = \frac{V_o(T)}{V_c(T_c)} \times \frac{R}{R + R_i(T)} = \frac{V^* + \beta T}{V^* + \beta T_c + I_c R_i(T_c)} \times \frac{R}{R + R_i(T)} \qquad (2)$$

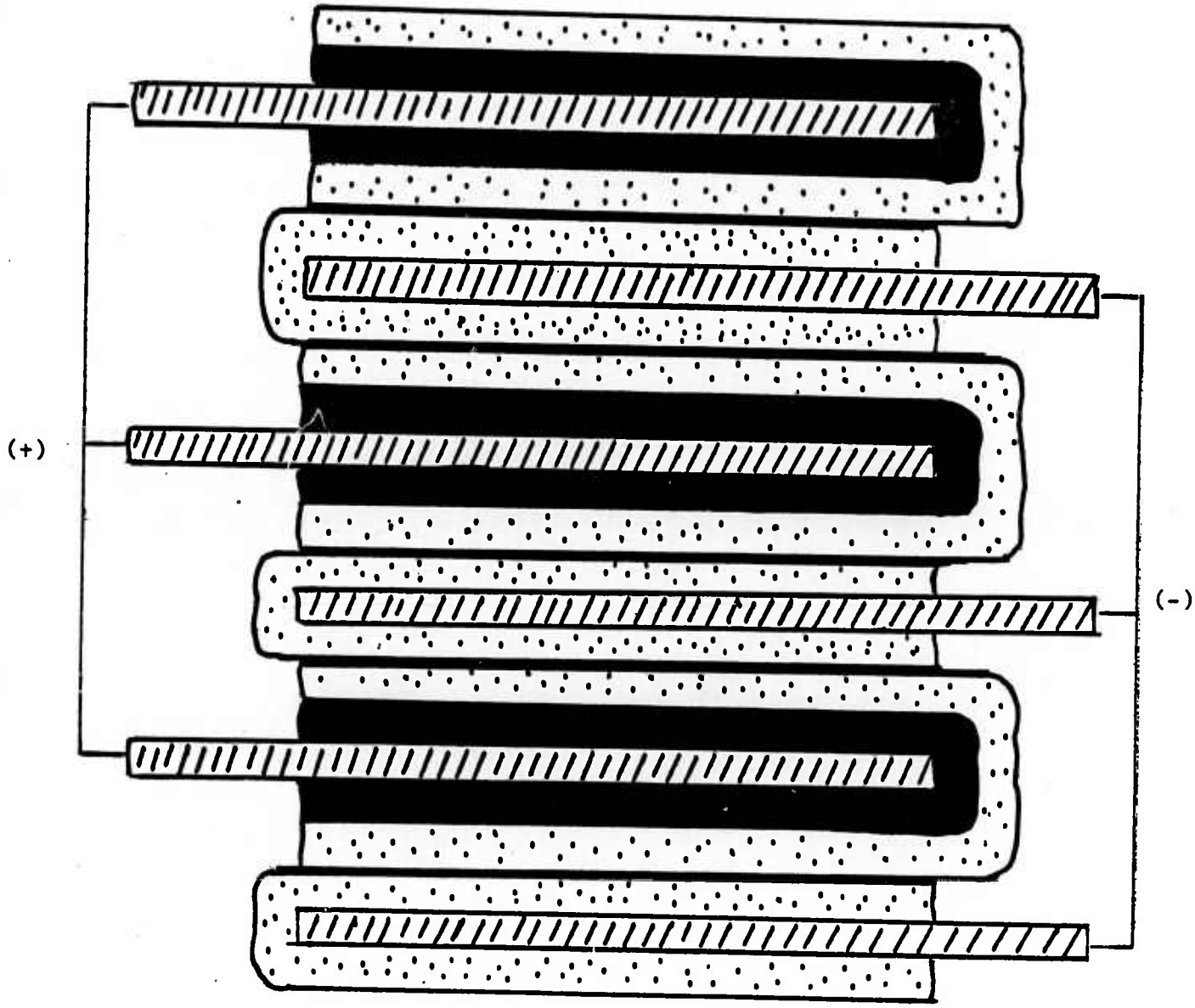
If we wish to discharge with maximum power density, then R - R_i, and the only way to keep the conversion efficiency high is to charge at room temperature while discharging at high temperature.

On the other hand, if we charge and discharge at the same temperature, the only way to achieve high conversion efficiency is to have R >> R.

APPENDIX 4

	"C" CELLS	"D" CELLS
Diameter	26mm	34mm
Height	50	61
Weights		
Zinc-Carbon	38g	95g
Alkaline	65g	127g
Nickel-Cadmium	80g($2.90)	160g($6.00)
Lithium	44-55g($6.50)$SO_2$ ($8.65)Thionyl Chloride	80-100g($7.70)$SO_2$ ($10.30)Thionyl Chloride

TPYE	VOLTS	mAh	WEIGHT	TEMP. RANGE
PRIMARY		"C" CELLS		
Zinc-Carbon	1.5	2,500	46g	
Alkaline	1.5	6,000	64.5	
Lithium:				
MnO_2	3	5,000	44	-40° to 85°C
SO^2	3	3,400	44	-53° to 73°C
Thionyl	3.6	6,000	56	-48° to 70°C
Thionyl Cl	3.7	5,000	52	-40° to 73°C
SECONDARY				
Ni-Cd	1.5	1,800	67	0 - 50°C -20° to 70°C extra cost
		"D" CELLS		
PRIMARY				
Zinc-Carbon	1.5	6,000	95	
Alkaline	1.5	13,000	127	
Lithium:				
SO_2	3.0	8,300	80	
Thionyl Cl	3.7	10,000	99	
Thionyl	3.6	14,000	115	
SECONDARY				
Ni-Cd	1.5	4,000	147	



LEGEND:

Aluminum

Graphite

Oxide

Fig.1 PARALLEL STACKED THERMOVOLTAIC CELL

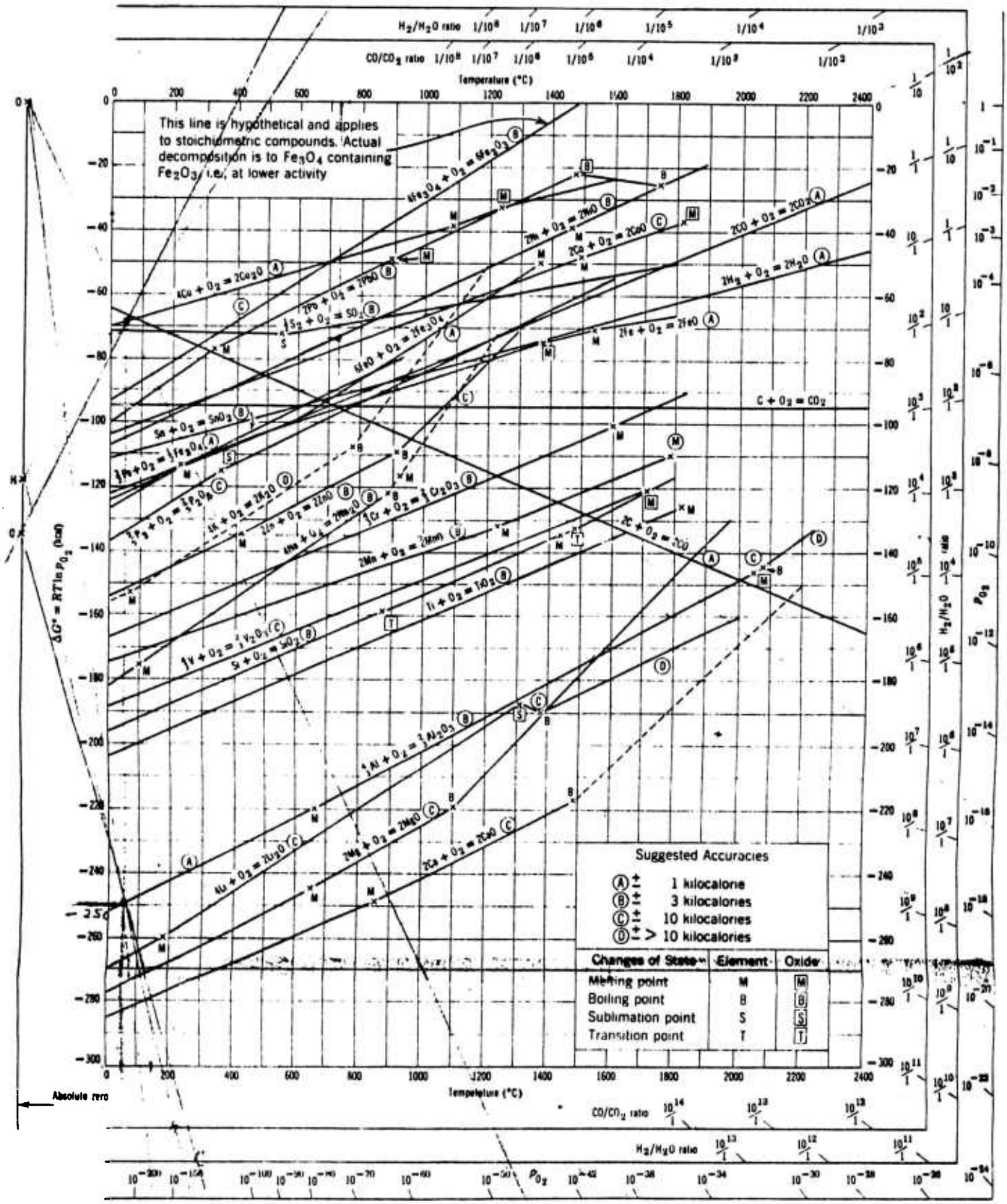


Fig. 7.7 Standard free energy of formation of oxides as a function of temperature. From F. D. Richardson and J. H. E. Jeffes, *J. Iron Steel Inst.*, 160, 261 (1948). Modified by L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York, 1953.

FIGURE 2

GRAPHITE/SALT SATURATED PAPER/ALUMINUM FOIL

VOLTS VS. MICROAMPERES

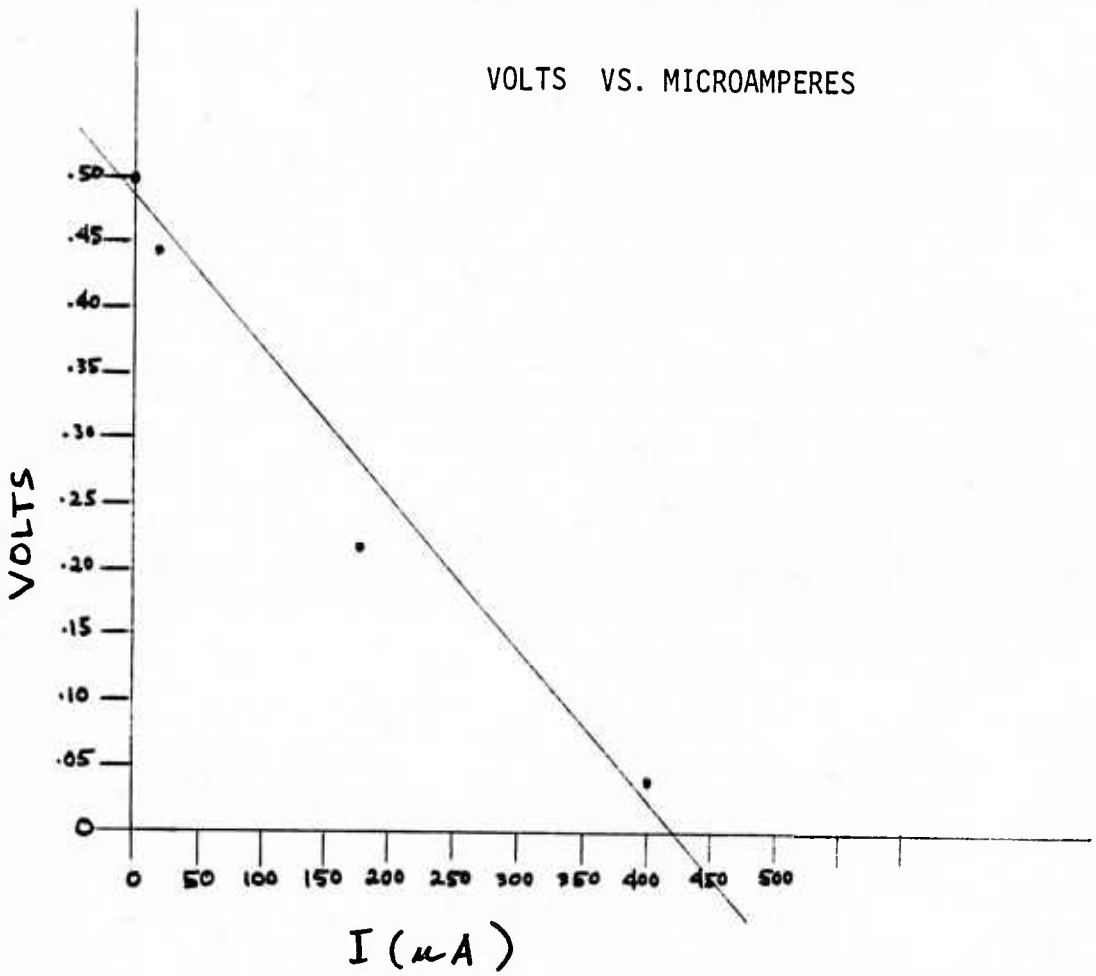


FIGURE 3

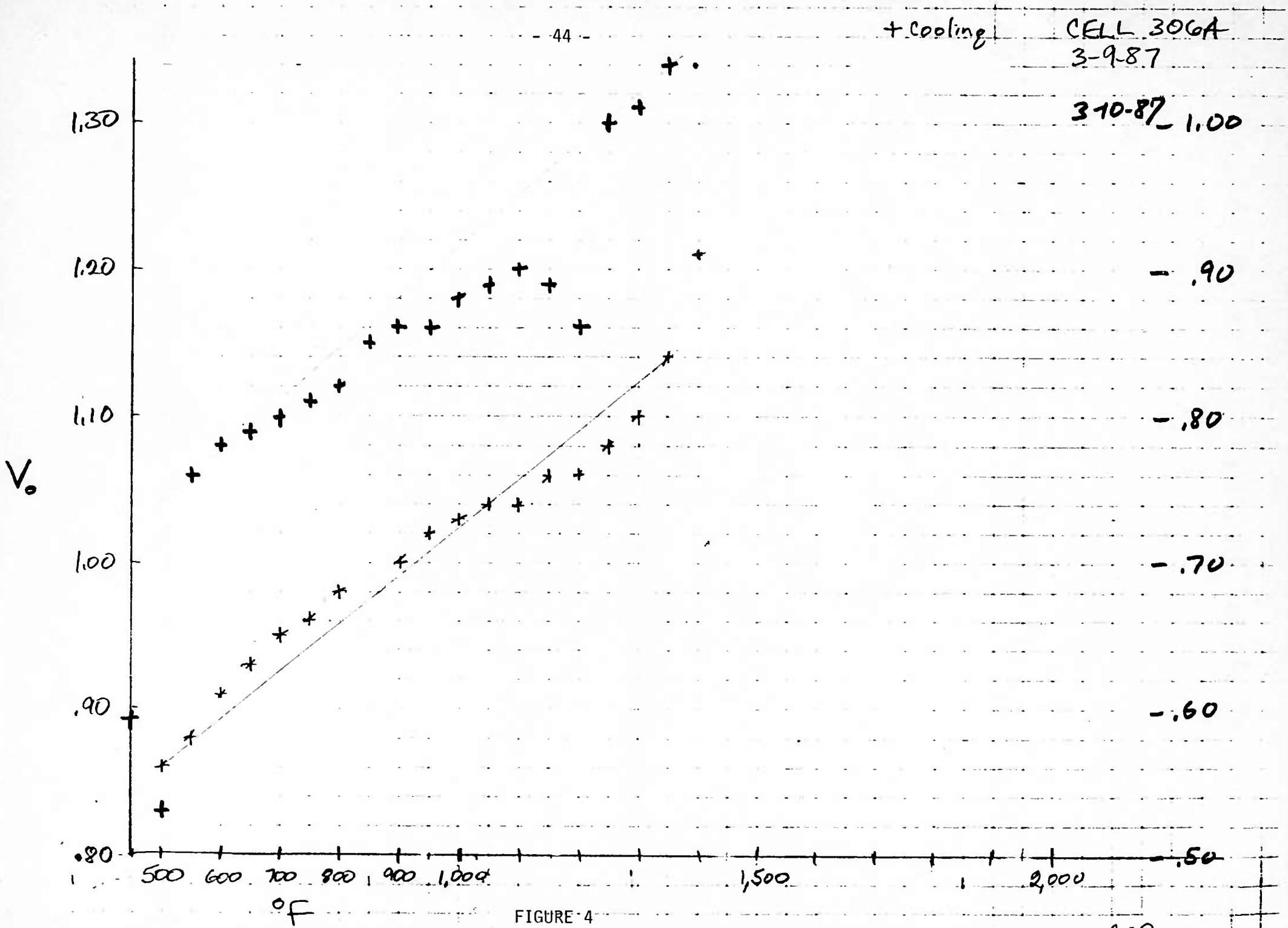
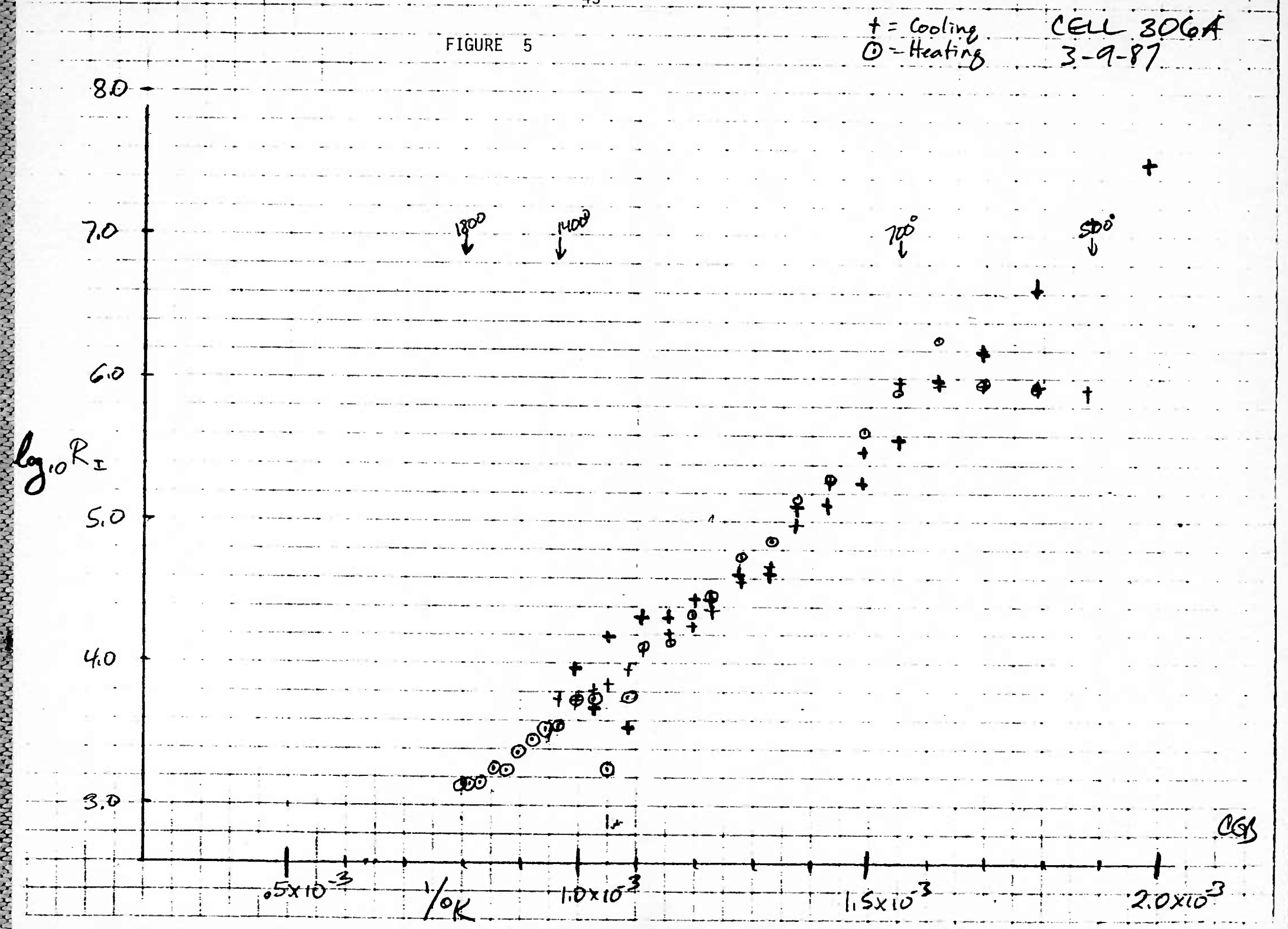

+ cooling
CELL 306A
3-9-87
3-10-87
1.30
1.20
1.10
1.00
.90
.80
V_o
1.00
.90
.80
.70
.60
.50
500
600
700
800
900
1,000
1,500
2,000
°F
CGB

FIGURE 4

FIGURE 5


+ = Cooling
⊙ = Heating
CELL 306A
3-9-87
8.0
7.0
6.0
5.0
4.0
3.0
$\log_{10} R_I$
1800°
1400°
700°
500°
.5x10^{-3}
1/°K
1.0x10^{-3}
1.5x10^{-3}
2.0x10^{-3}
CGB

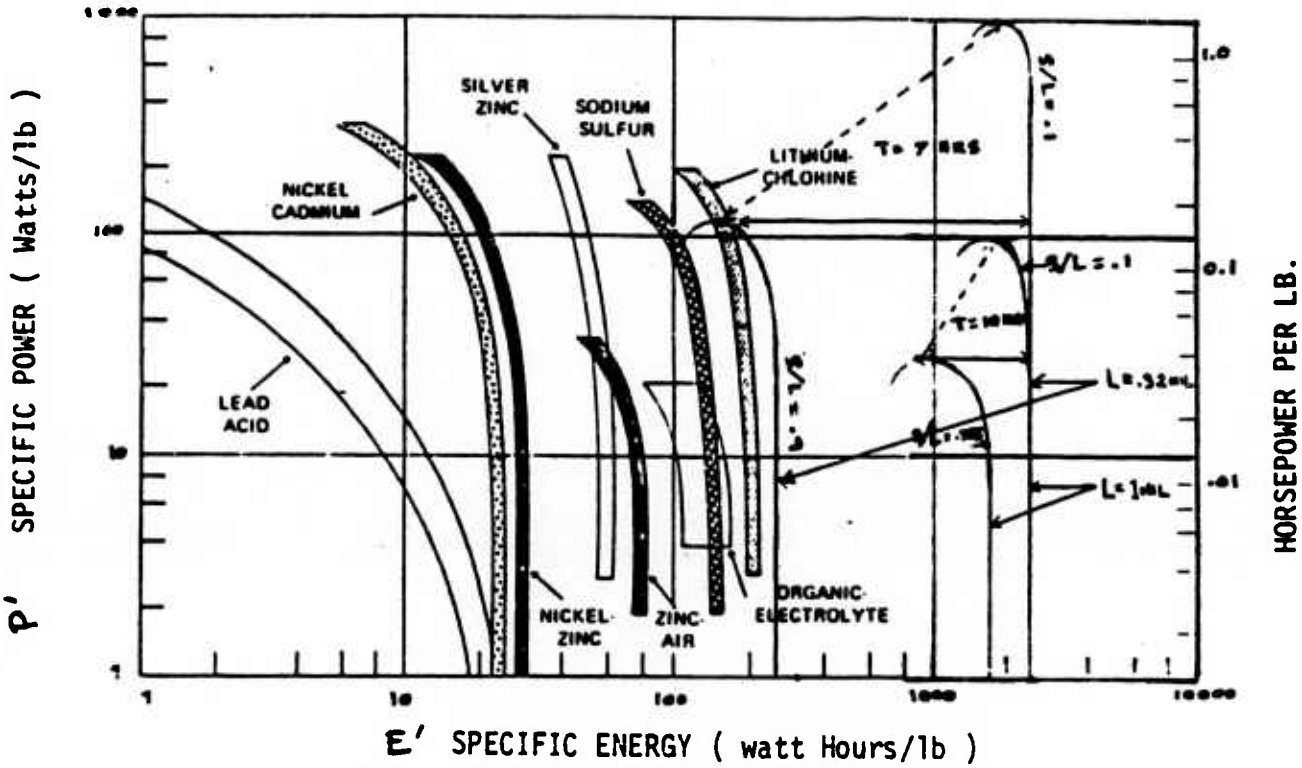


Fig.1 A comparison between practical specific energy characteristics of the lead-acid storage battery and other systems. (Batteries: Vol. 2 (1977) by Karl V. Kordesch)

FIGURE 6

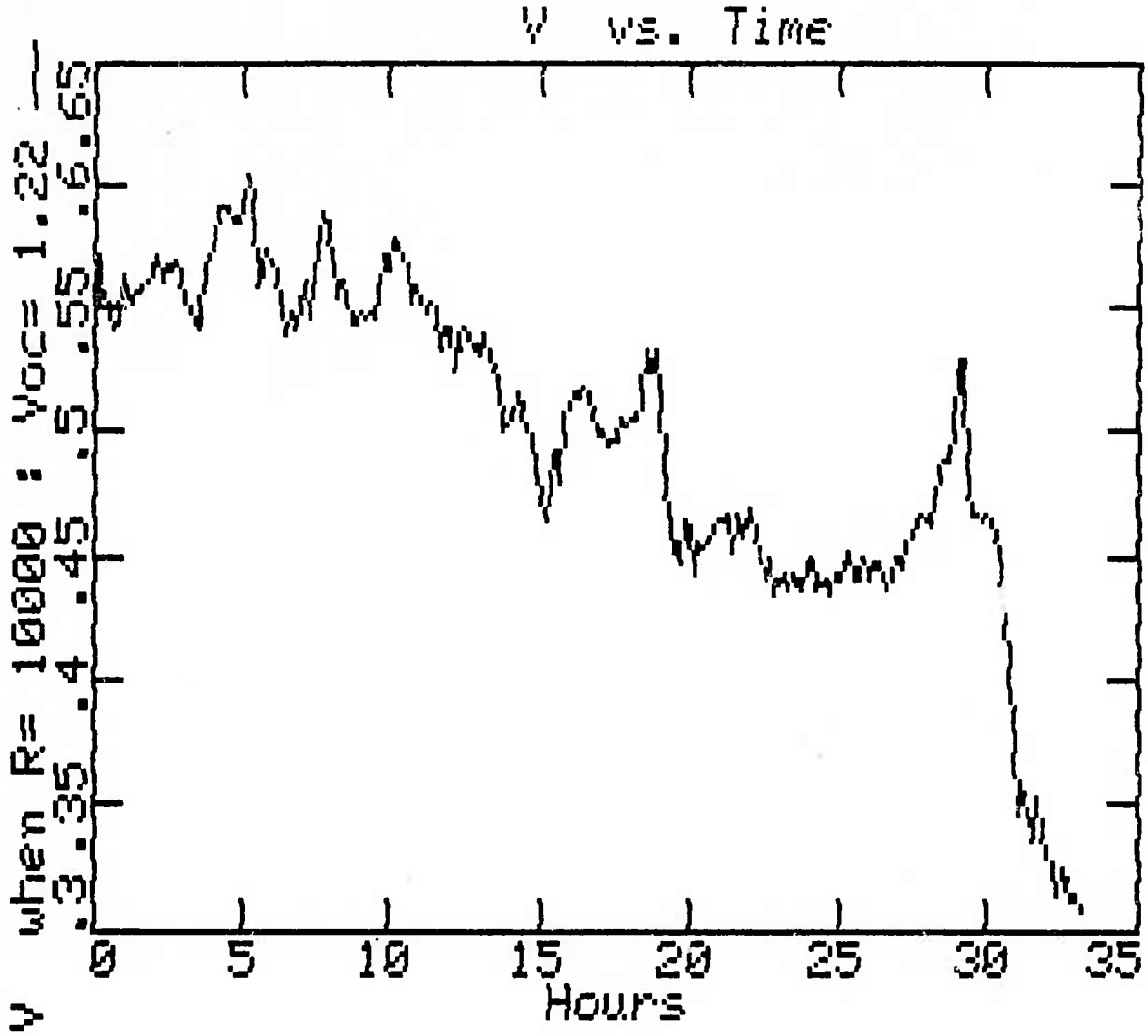

V vs. Time
V when R= 10000 : Voc= 1.22
.3 .35 .4 .45 .5 .55 .6 .65
0 5 10 15 20 25 30 35
Hours

FIGURE 7A

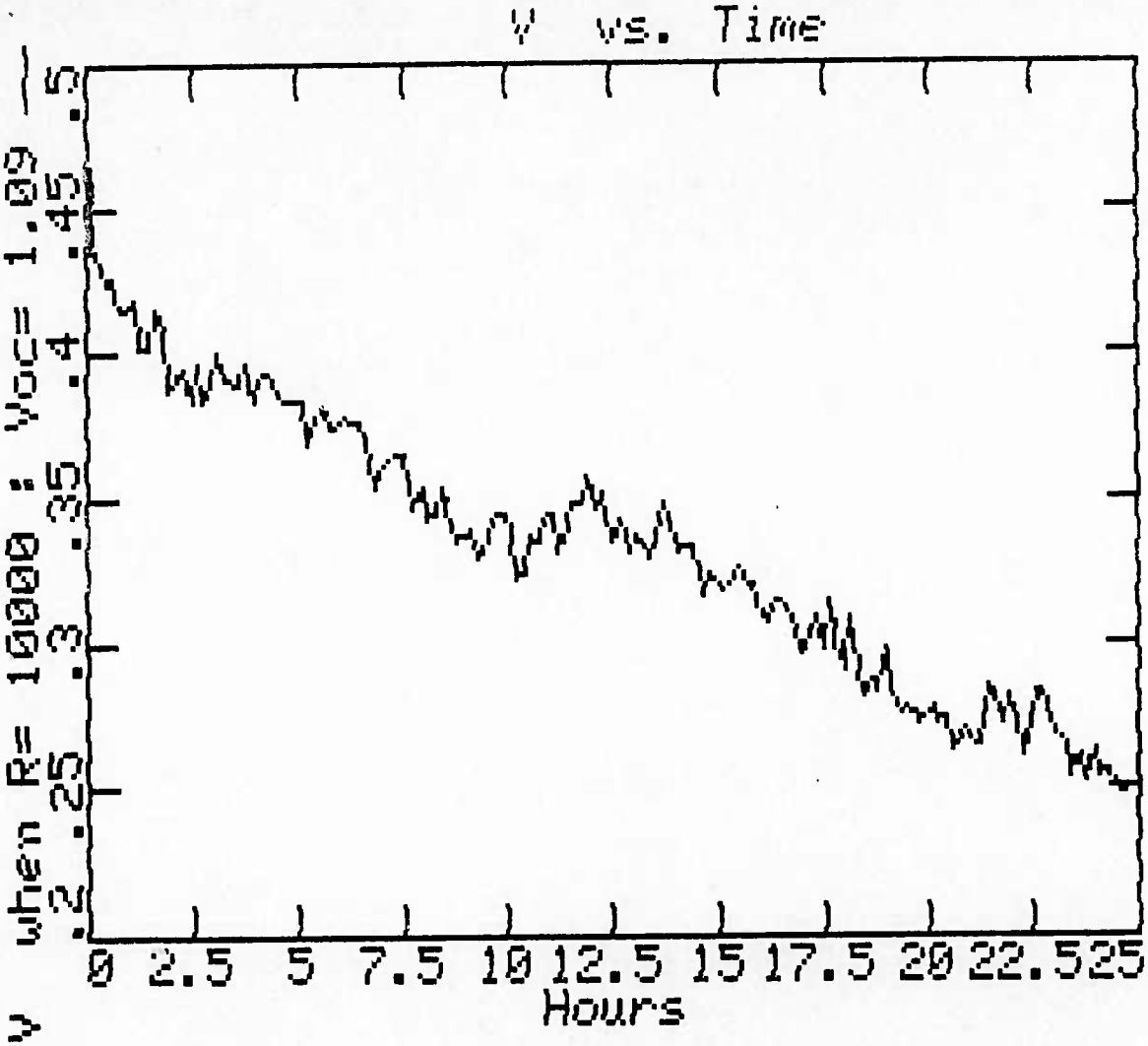

V vs. Time
V when R= 10000 : Voc= 1.09
.2 .25 .3 .35 .4 .45 .5
0 2.5 5 7.5 10 12.5 15 17.5 20 22.525
Hours

FIGURE 7B

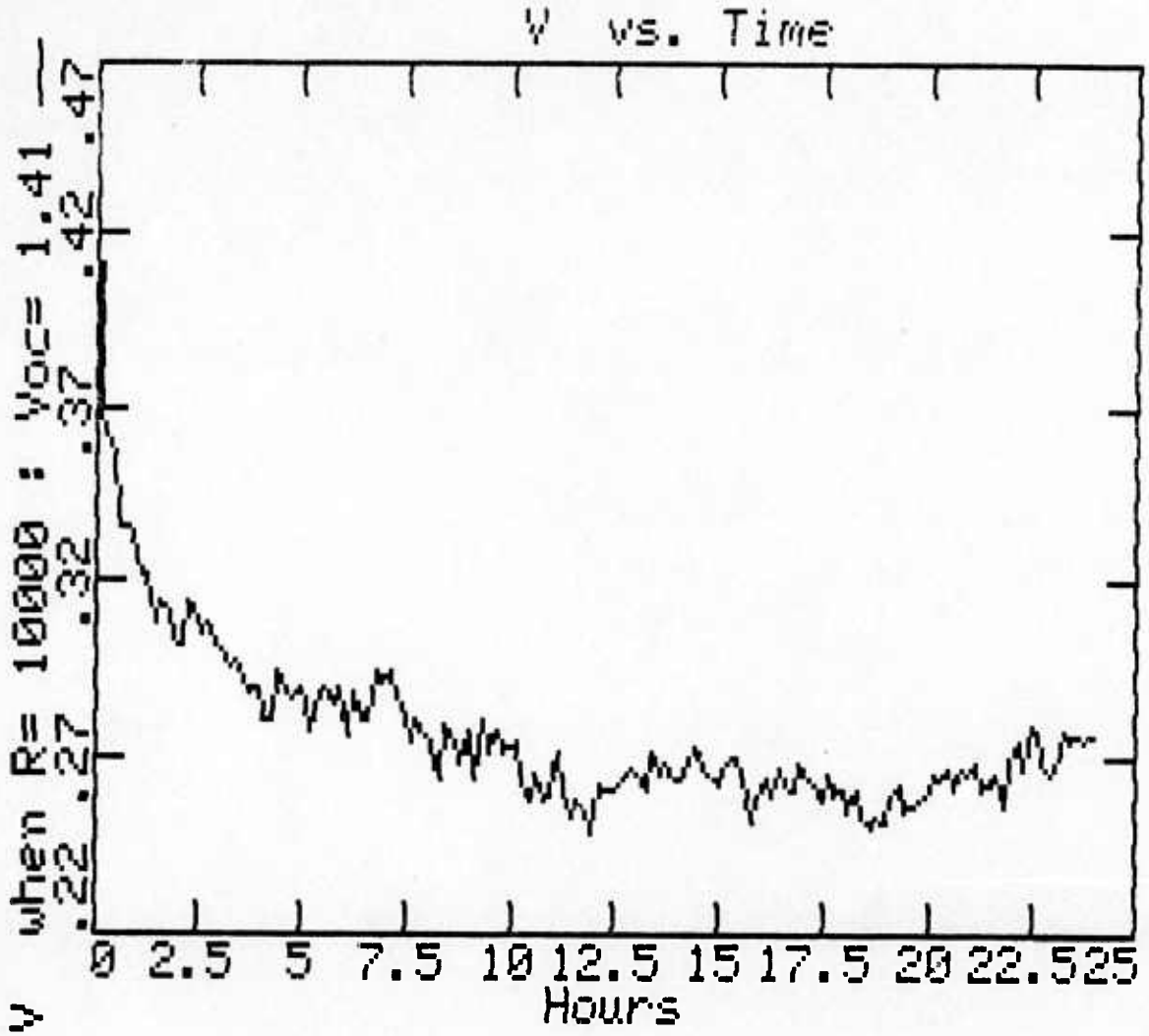

V vs. Time
V when R= 10000 : Voc= 1.41
.22 .27 .32 .37 .42 .47
0 2.5 5 7.5 10 12.5 15 17.5 20 22.525
Hours

FIGURE 7C

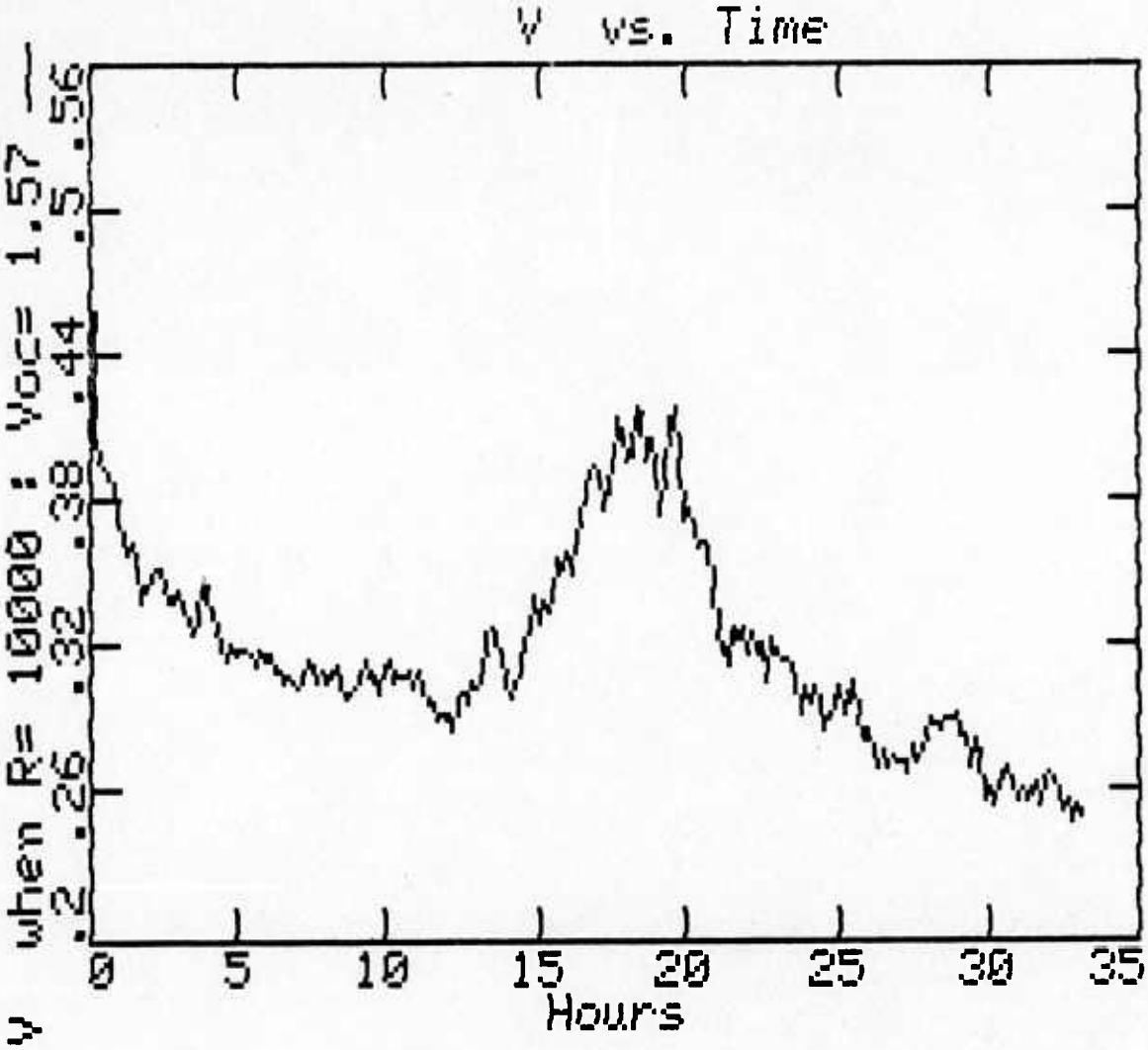

V vs. Time
V when R= 10000 : Voc= 1.57
.2
.26
.32
.38
.44
.5
.56
0
5
10
15
20
25
30
35
Hours

FIGURE 7D

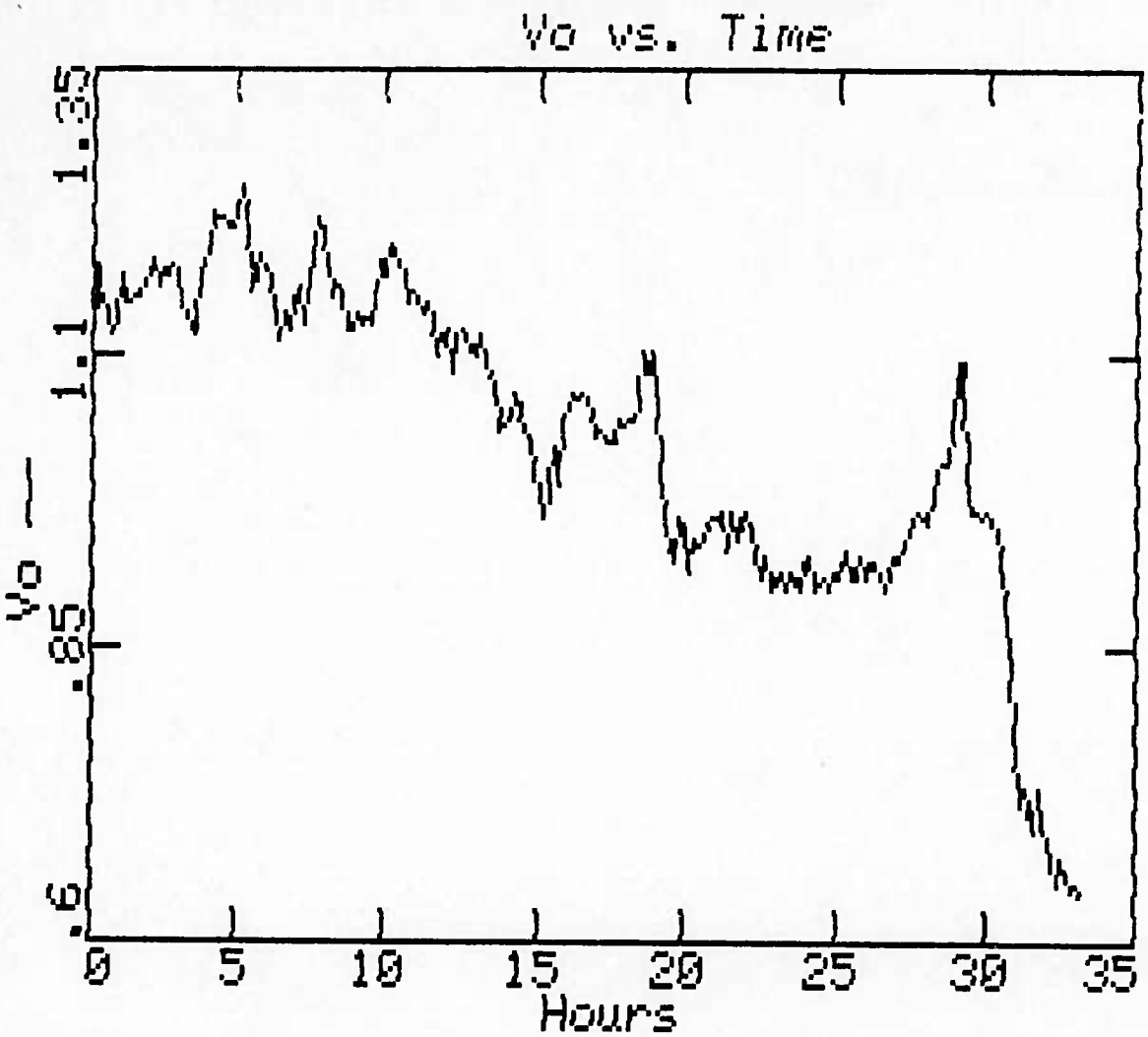


FIGURE 8A

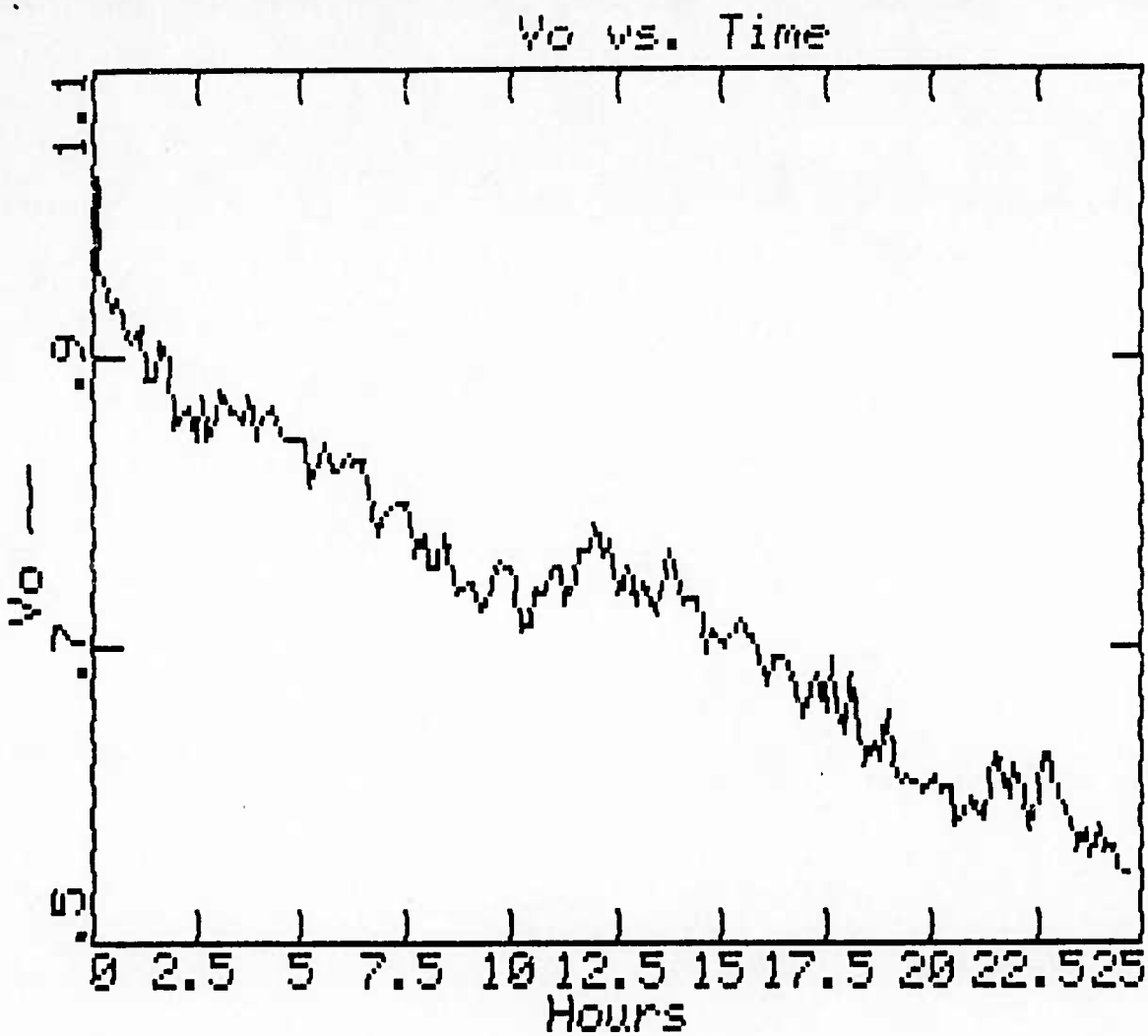


FIGURE 8B

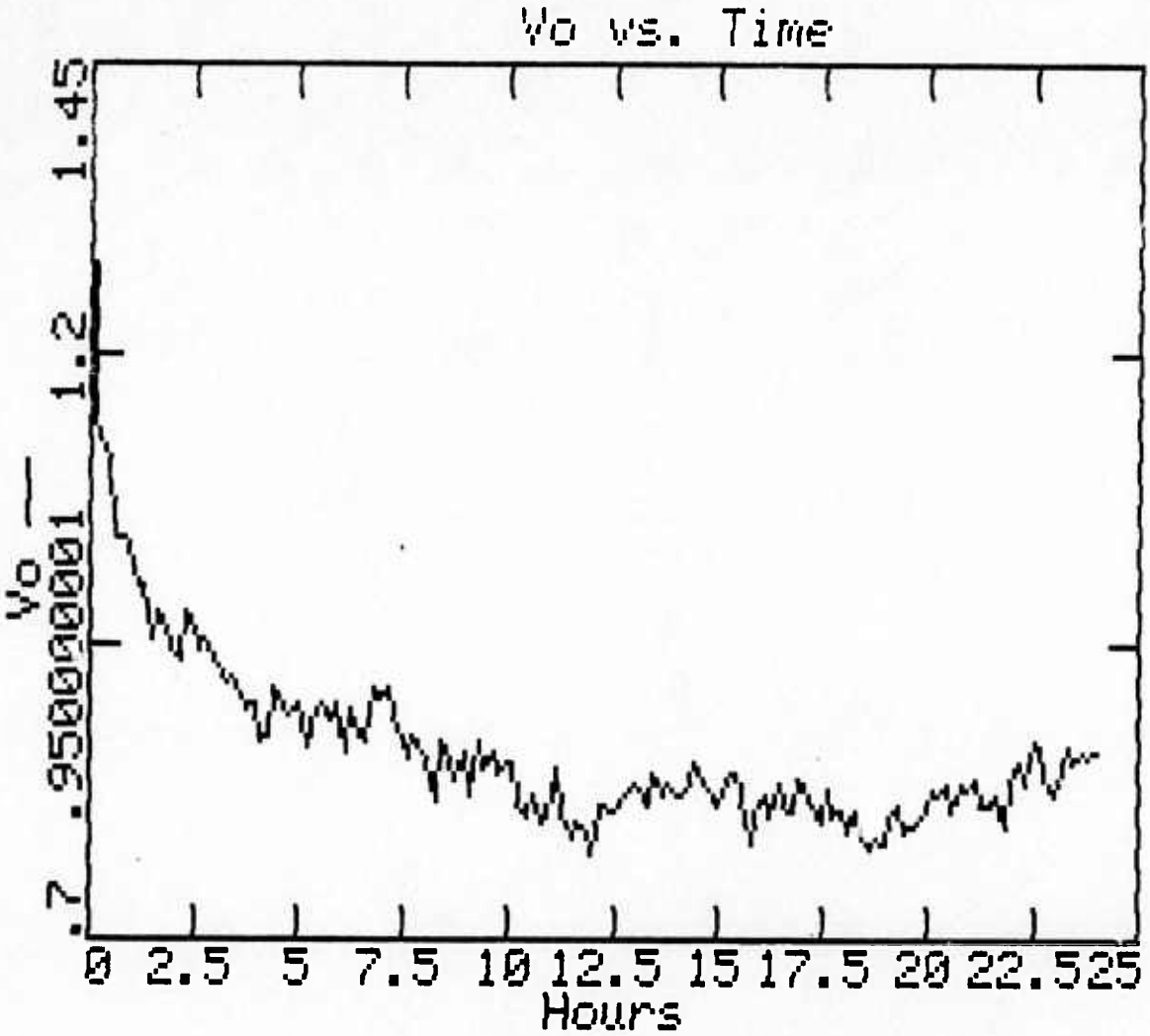

Vo vs. Time
Vo
1.45
1.2
.9500000001
.7
0
2.5
5
7.5
10
12.5
15
17.5
20
22.525
Hours

FIGURE 8C

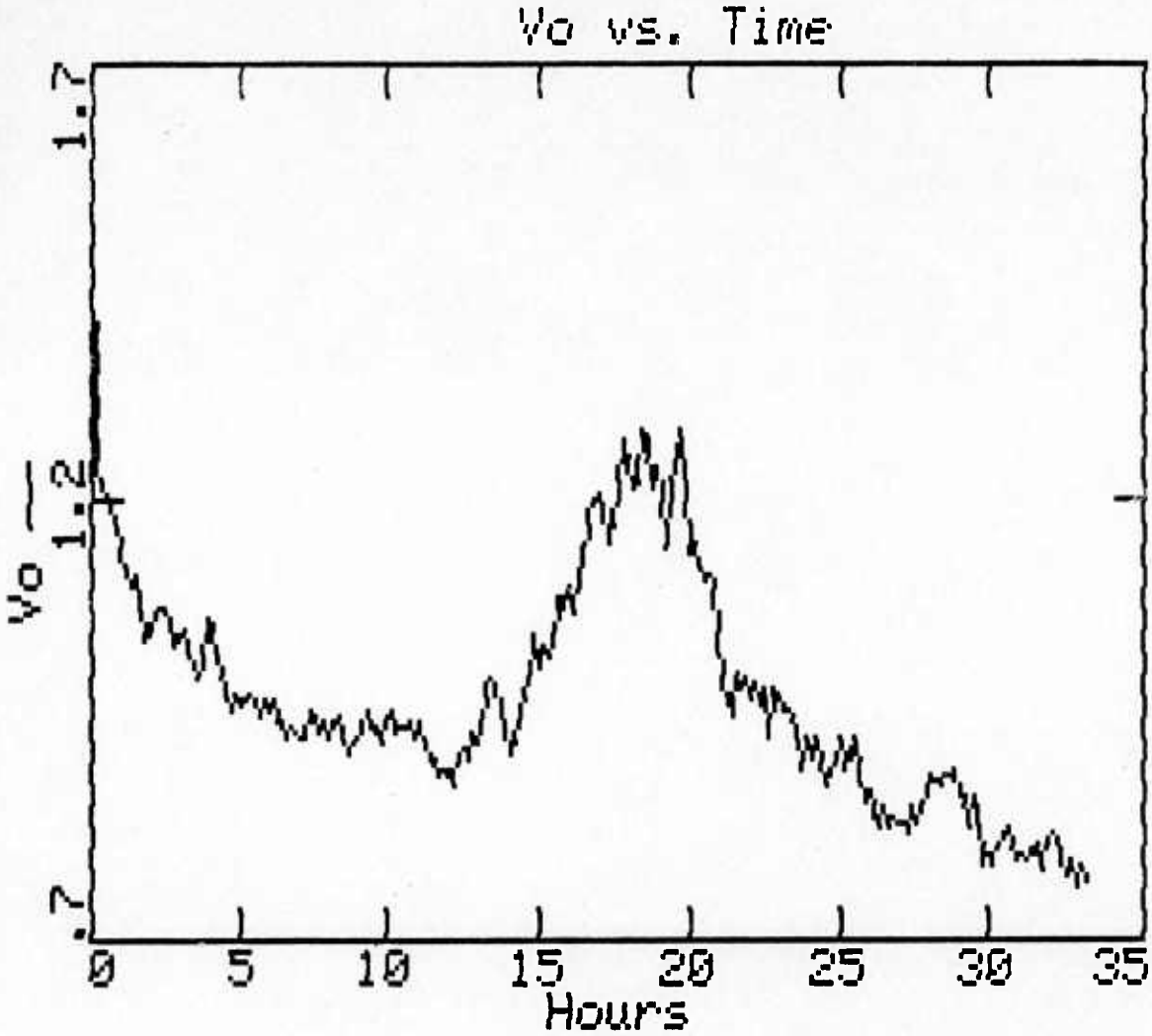


FIGURE 8D

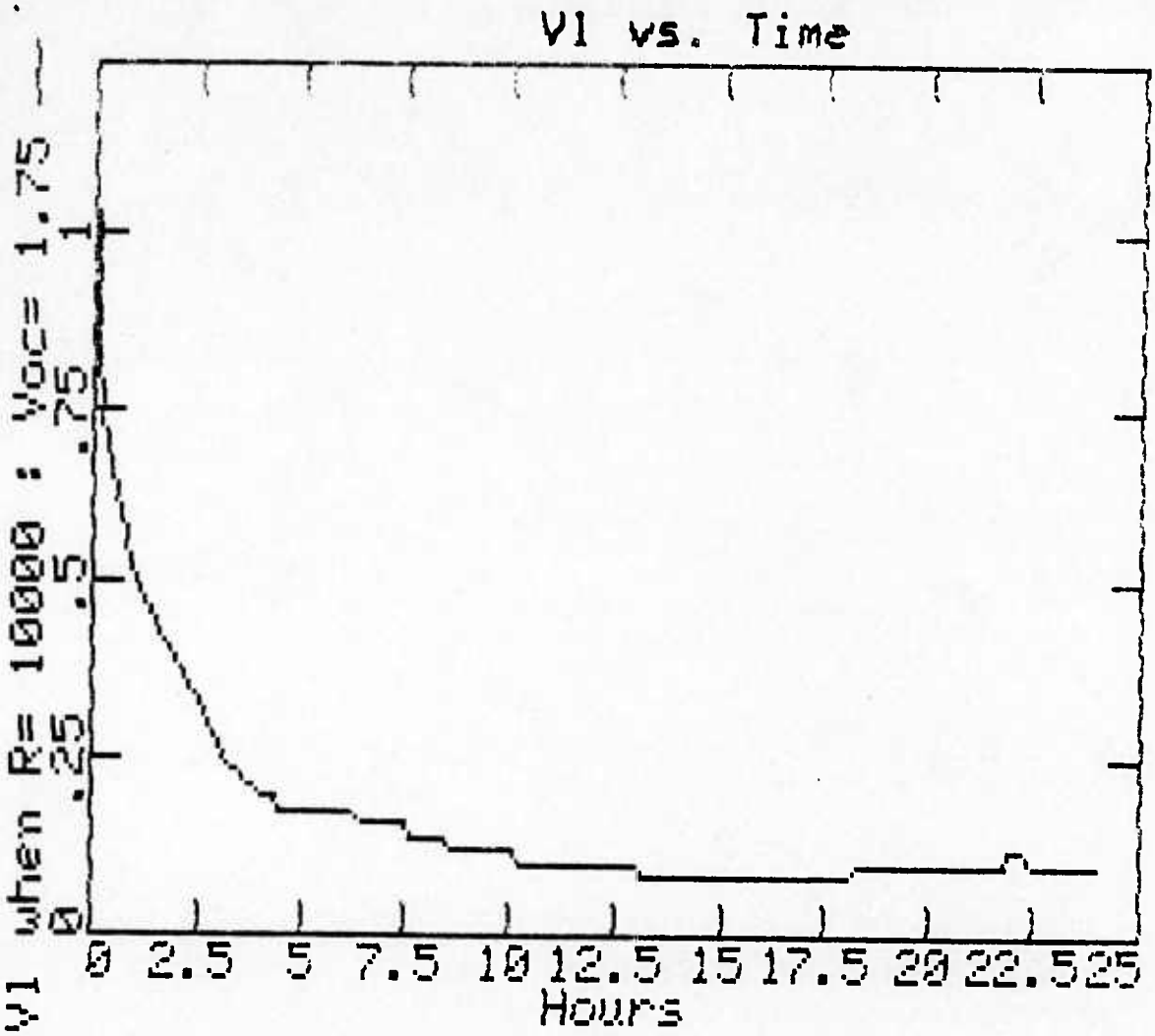

V1 vs. Time
V1 when R= 10000 : Voc= 1.75
0
.25
.5
.75
1
0 2.5 5 7.5 10 12.5 15 17.5 20 22.5 25
Hours

FIGURE 9A

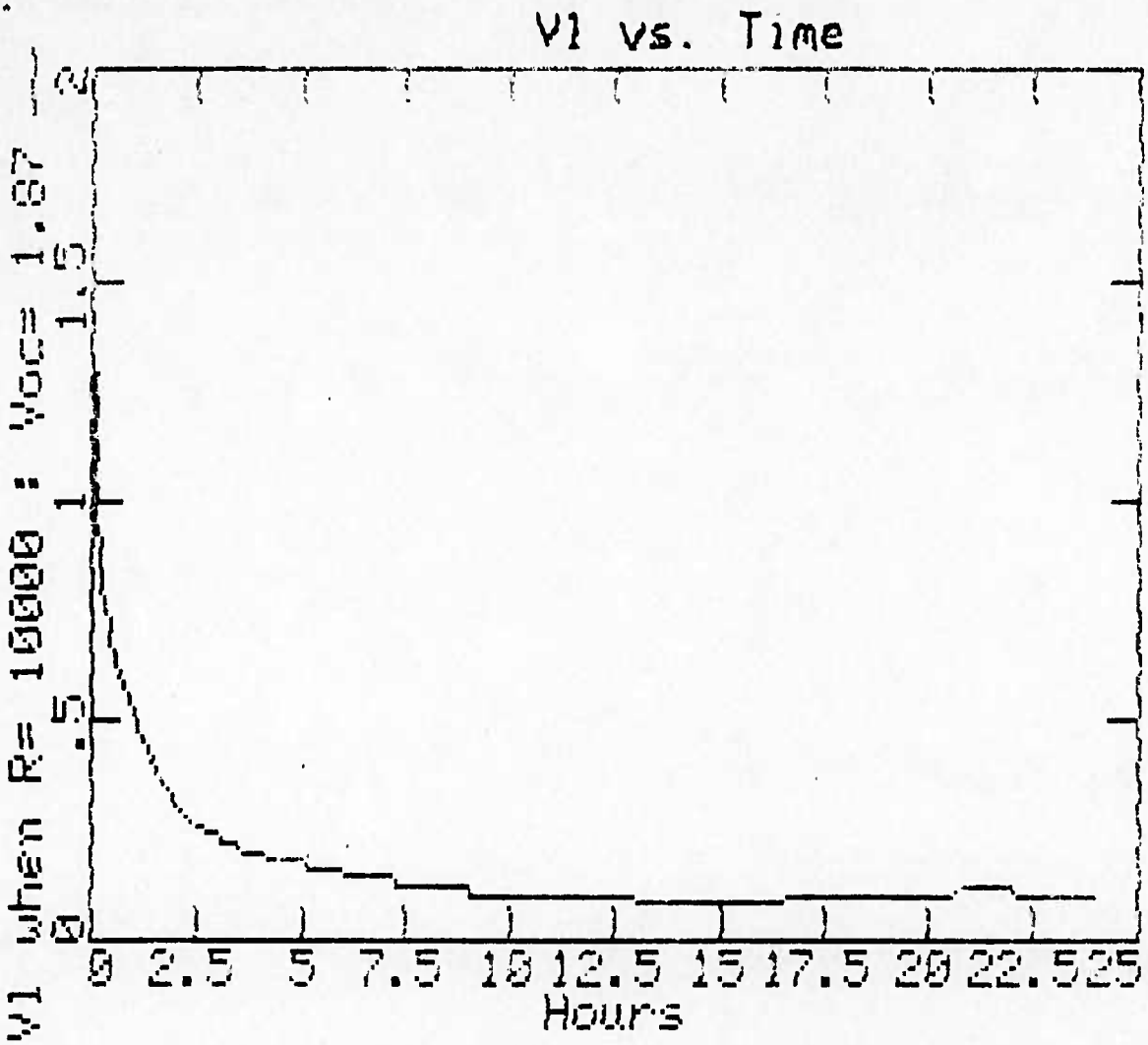

V1 vs. Time
V1 when Re= 100000 : Wocc= 1.87
0
.5
1
1.5
2
0 2.5 5 7.5 10 12.5 15 17.5 20 22.525
Hours

FIGURE 9B

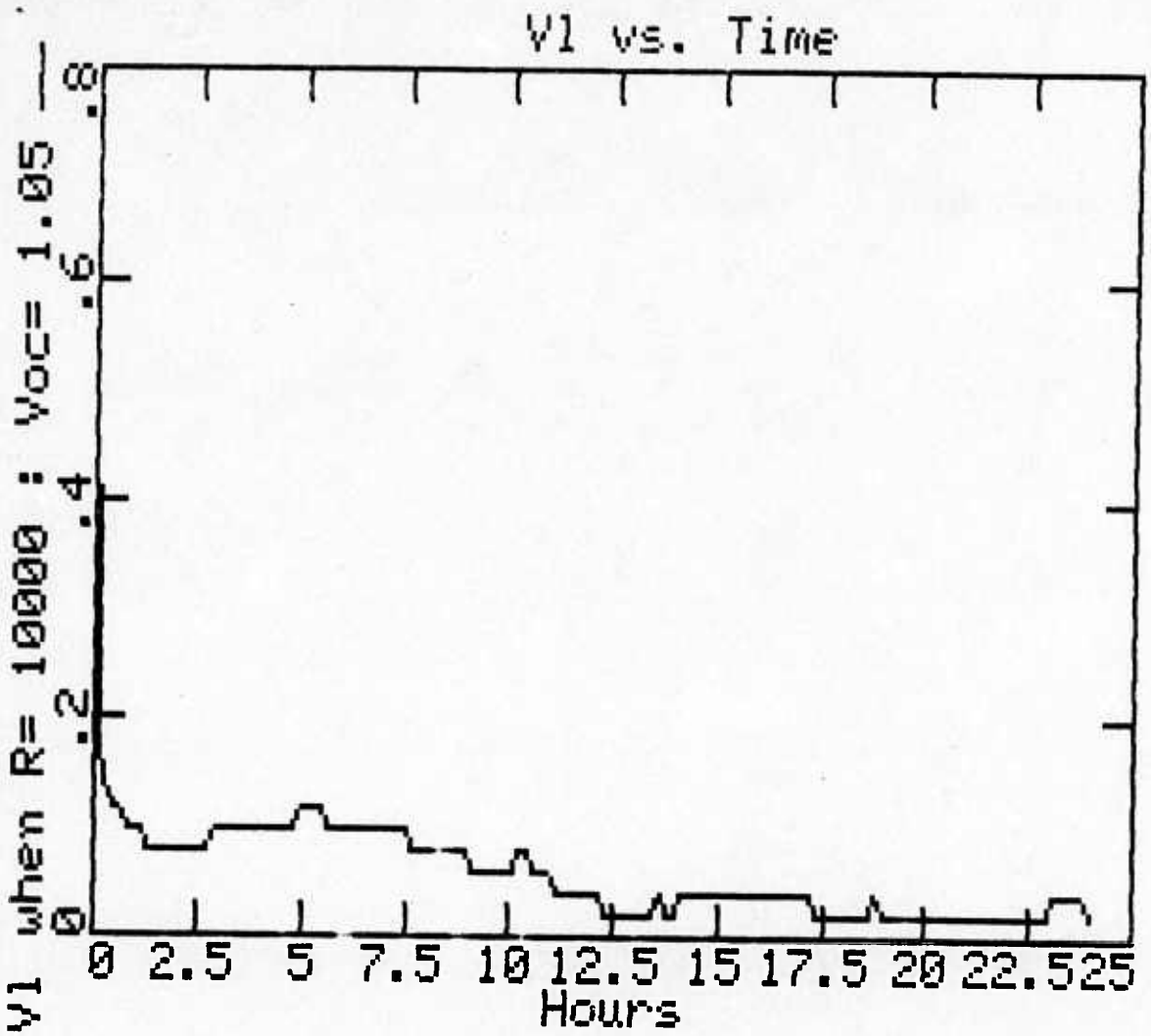
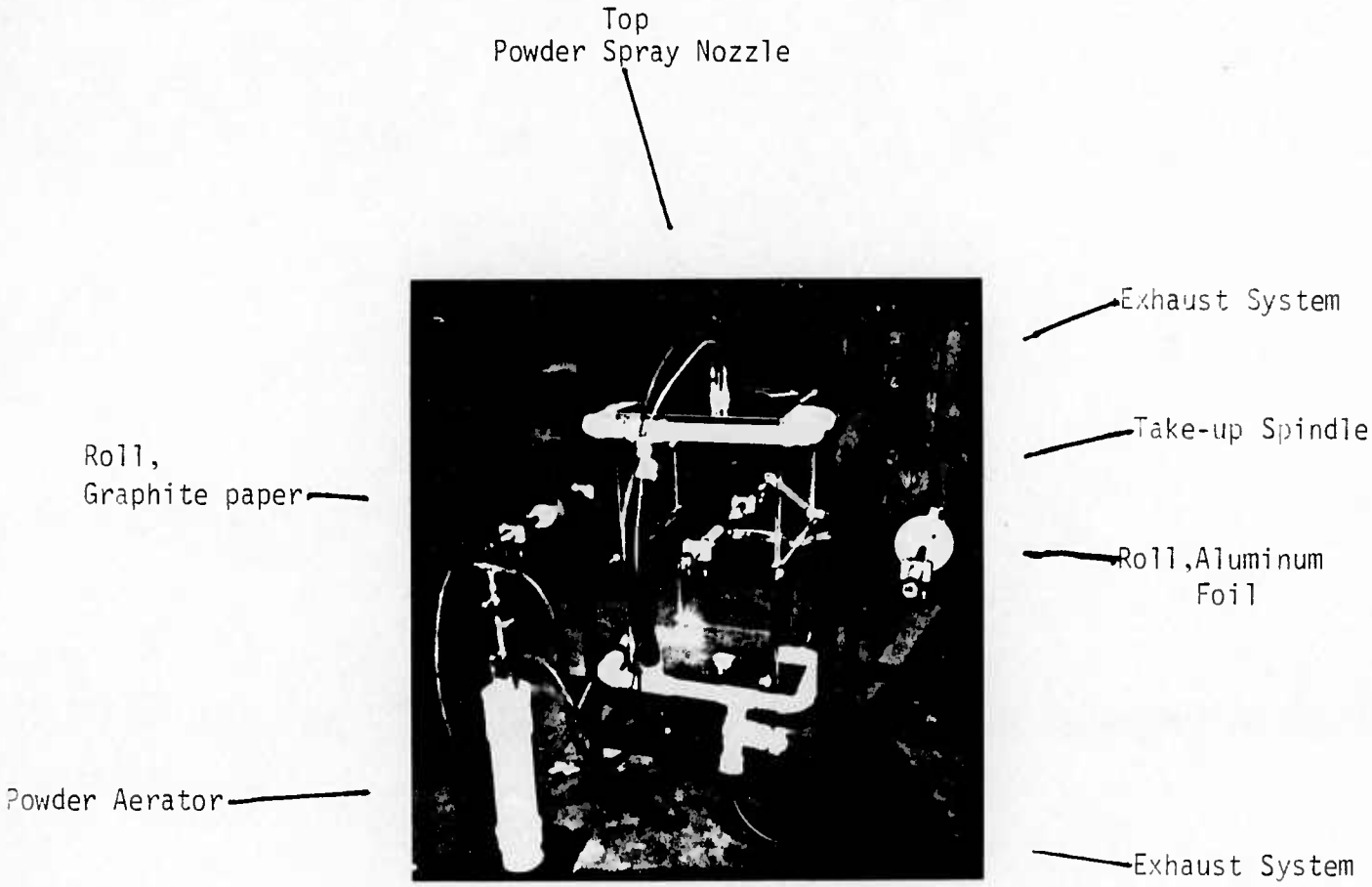

V1 vs. Time
V1 when R= 10000 : Voc= 1.05
0
.2
.4
.6
.8
0 2.5 5 7.5 10 12.5 15 17.5 20 22.525
Hours

FIGURE 10

FIGURE 11 BATTERY WINDING MACHINE



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