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ELECTROCHEMISTRY OF SOME NEW ALKALINE BATTERY ELECTRODES

FEBRUARY 1976

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INTERIM REPORT

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This report contains results of efforts to develop new alkaline battery electrodes for use in cells such as nickel-cadmium, nickel-zinc and silver-zinc. Work was performed in the Aerospace Power Division (POE-1) of the Air Force Aero-Propulsion Laboratory, Wright-Patterson AFB, Ohio under Project 3145, Task 314522, and Work Units 31452240, 31452267, 31452263. The efforts were conducted by Dr. David F. Pickett, Mr. Wayne S. Bishop, and Mr. Richard A. Marsh, respectively.

This report has been reviewed by the Information Office (ASD/OIP) and releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations. It is being given as a paper at the 1975 Pacific Conference on chemistry and Spectroscopy in Los Angeles, California.

This technical report has been reviewed and is approved for publication.

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New alkaline battery electrodes used in cells such as nickel oxide-cadmium, nickel oxide-hydrogen, nickel oxide-zinc, and silver oxide-zinc have been developed as a result of contracted and in-house research at the Air Force Aero-Propulsion Laboratory. Cathodic hydroxide precipitation techniques are used for preparation of nickel oxide and cadmium electrodes. Bipolar silver oxide-zinc electrodes are fabricated by spray deposition-sintering and vapor deposition techniques. Novel methods for preparation of dry charged nickel

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oxide electrodes for reserve type nickel oxide-zinc batteries are being investigated. One technique involves charging conventional sintered, vacuum impregnated electrodes then removing electrolyte with a distilled water wash. Drying is performed *in vacuo*. The plates yield rated capacity upon activation, but no long term dry storage data is available. Secondary nickel oxide electrodes, prepared by Cathodic precipitation techniques, appear far superior to other nickel oxide electrodes because of their reduced thickening with charge-discharge cycling at deep depths of discharge and their good charge acceptance at high temperatures. The silver oxide-zinc electrode fabrication techniques have made construction of a multicell pile for high power applications feasible. Minor problems such as anomalous gassing have been incurred but appear capable of solution. For the zinc electrode, material utilization factors of 650, 680 and 600 ampere-seconds per gram have been recorded at current densities of 1.5, 1.75 and 2.0 amps/inch^2, respectively.

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INTRODUCTION

Developments in storage batteries have been slow in comparison to other areas of energy conversion. This is especially true in the field of alkaline batteries. There are a number of reasons for the meager progress, but without enumerating these, it should be mentioned that many of the breakthroughs were made by tireless individuals such as Edison, Jungner and Andre'. An excellent review of their work is given in the book by Falk and Salkind[1].

The first alkaline battery, the Lelande-Chaperon cell, was patented in 1884. Soon afterwards there were a number of variations described in the patent literature, but a modification by Edison in 1889, the Edison-Lelande cell, was by far the most successful. A modern day version is still used in railroad signaling applications. It was only recently that production of this copper oxide-zinc battery was terminated by the Edison Storage Battery Division of the McGraw-Edison Co.

In 1909 manufacturing of nickel-cadmium pocket plate cells began in Sweden, and almost twenty years later sintered plates were developed in Germany for nickel-iron and nickel-cadmium cells[2]. The first military production occurred in the 1930s, and variations of the sintering and impregnation processes are still in use today throughout the battery industry.

The first successful silver-zinc battery did not emerge until

[1] S.U. Falk and A.J. Salkind, Alkaline Storage Batteries, John Wiley and sons, New York, 1969.

[2] G. Pfleiderer, F. Spaun, P. Gmelin, K. Ackermann, German Patent 491,498 (1928).

1941, after over twenty years of work on the system by Andre'[3]. Its success is mainly attributed to development of a cellophane separator which kept the colloidal silver oxide particles from migrating to the negative plate.

Spin-offs from the space program are responsible for many of the present day improvements that we have in alkaline batteries such as Hermetically sealed nickel-cadmium cells and vastly improved silver cells.

Military programs have also played a definite role in many of the current developments in alkaline battery technology. Some of the recent progress at the Air Force Aero-Propulsion Laboratory in electrode fabrication is given in this report. Techniques in electrochemical impregnation of sintered nickel plaque with cadmium and nickel hydroxide have been developed in-house which have demonstrated vastly superior performance over electrodes presently used in nickel cadmium cells. This nickel hydroxide electrode is a logical candidate over other nickel hydroxide electrodes for the nickel hydrogen cell. Due to investigations for a charged dry stand nickel hydroxide electrode, a reserve type nickel zinc system appears feasible for replacement of the costly silver-zinc batteries presently used in primary missile batteries. Finally, high power, on the order of megawatts, appears a definite reality for aircraft applications as a result of a development program for a bipolar electrode, pile type silver-zinc battery.

[3] H. Andre', Bull. Soc. Franc. Electriciens, (6), 1, 132 (1941)

IMPROVED SECONDARY NICKEL-CADMIUM CELLS

Nickel-Cadmium batteries have been in commercial production over sixty years. The earliest versions had an energy density of about four to five watt-hours a pound and could be charged and discharged in 45 minutes.[4] Welding was not fully developed; therefore, methods of construction were mostly dependent upon mechanical means of assembly. In contrast, space-age technology has provided means of producing nickel-cadmium cells that can store and deliver up to five times the electrical energy in a few minutes for the same weight. Needless to say, these batteries are much sturdier in construction than the early models. This modern day version which is the power storage device in practially all U.S. Air Force satellites and aircraft is known as a sintered plate nickel-cadmium battery.

The first sintered plate cells were developed during the late 1920s at the I.G. Farben industrie A.G. in Germany.[5] Cells using this design were not put into production to any extent until almost ten years later during the early stages of World War II. Sintered plates have a large active surface area, can be made unusually thin, and may be placed very close together. These features give rise to good high rate performance. This characteristic, along with their excellent low temperature performance, made sintered plate nickel-cadmium cells excellent candidates for military applications.

4 Waldemar Junger, Swedish Patent 15,567 (1901), German Patent 163,170 (1901). See S.U. Falk and A.J. Salkind, Alkaline Storage Batteries, John Wiley and Sons, New York, 1969, p. 16.

5 G. Pfleiderer, F. Spaun, P. Gmelin, K. Ackermann, op. cit.

Prior to development of the sintered plaque electrode, active material in the plates was held in folded pockets of thin, perforated copper or nickel-plated steel sheets. Graphite was sometimes added to enhance conductance of the metal oxides and hydroxides. The porous sintered plaque replaced the pockets yielding a substrate that retained the active material while collecting and conducting the electric current. The plaque is prepared by sintering a high surface area nickel powder with a centrally located expanded nickel grid, wire screen, perforated nickel or nickel plated steel sheet.

Sintering is a process through which a mass of particles having the approximate same composition is transformed into a ridged body without reaching the melting point of the material. In general, the process is possible because of the ability of metals and other solids to exhibit some bulk and surface mobility. Although surface tension appears to constitute the principal driving force, the subject is actually a rather complex one and not fully understood.[6] Sintering of metal powders, such as iron or nickel, under proper conditions produces a continuous porous, conducting matrix which can be impregnated with active materials.

The active material in a nickel-cadmium battery is nickel (III) hydroxide (NiOOH) in the positive plate and cadmium metal in the negative. On discharge these are converted to nickel (II) hydroxide ($Ni(OH)_2$) and cadmium hydroxide ($Cd(OH)_2$), respectively. The electrolyte used is 30-34% potassium hydroxide. Equations representing the half-reactions for these

[6] Arthur W. Adamson, Physical Chemistry of Surfaces, Interscience, New York, 2nd Ed., 1967, p. 263.

processes at each electrode are shown below:

$$Ni(OH)_2 + OH^- \underset{Discharge}{\overset{Charge}{\rightleftharpoons}} NiOOH + H_2O + e^-$$

$$Cd + 2OH^- \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} Cd(OH)_2 + 2e^-$$

Actually these equations are not fully representative of all phenomena occurring on charge and discharge in a nickel-cadmium battery. In fact, the physics and chemistry of a nickel-cadmium battery are quite complicated and not fully understood, and investigations are still being carried out in order to better elucidate the reactions occurring at the electrodes.

New Methods of Plate Manufacture

There is also a great deal to be learned about impregnating nickel plaques with active material. In the original development of the sintered electrode the active material was introduced by dipping the sintered plaques in solution of suitable metal salts, such as nitrates, followed by precipitation of the metal hydroxides by means of alkaline solution. Variations of this method are still used today which include the use of vacuum to increase the amount of nitrate salt drawn into the pores of the plaque and a cathodization treatment in hot alkali to remove residual nitrates by converting them to ammonia which is volatilized. This process requires a number of repetitions to fully load a plaque with active material. An alternate method for impregnation uses heat to transform the metal salts absorbed in the plaque to oxides or hydroxides.

In addition to the above methods of impregnation there are several other methods which are being developed. The most promising of these use electrochemical deposition in boiling nitrate solutions to deposit the active material inside the pores of the plaque. Using this technique a plaque may be fully impregnated within 10 minutes to a couple of hours depending upon the nature of solvent, boiling temperature and current density.

The first of these techniques was developed by R.L. Beauchamp at Bell Telephone Laboratories,[7] and involved the use of boiling aqueous solutions. Using scanning electron microscope techniques, Beauchamp has shown that a much more uniform distribution of active material is achieved throughout the plaque than with conventional vacuum-alkali impregnation methods.[8] Electrodes fabricated using this electrochemical method show a substantial improvement in capacity and retention of capacity with increasing cycle life. In the Bell Telephone process the plaque is made cathodic (the negative electrode of an electrolysis cell) in a boiling solution of nickel or cadmium nitrate and sodium nitrite using inert anodes. A current of about 0.5 amperes per square inch of plaque is applied for 30 minutes to one and one-half hours resulting in a fully impregnated plaque. Impregnation using state-of-the-art methods requires six to eight hours.

Similar methods of impregnation have been developed at the Air Force Aero-Propulsion Laboratory.[9] These methods differ from the Bell method in that an ethanol solution is used for impregnation of the positive plate and high current density is used for impregnation of the negative plate. Positive electrodes impregnated from the AFAPL process have a capacity of 9 to 10 ampere-hours per cubic inch as opposed to about 5 ampere-hours per cubic inch for state-of-the-art. A fully impregnated negative plate may

[7] R.L. Beauchamp, U.S. Patent 3,573,101; U.S. Patent 3,653,967.

[8] R.L. Beauchamp, J. Electrochemical Society, to be published.

[9] David F. Pickett, U.S. Patents 3,827,911 (Aug 1974); 3,873,368 (Mar 1975).

be obtained in less than 10 minutes using the AFAPL technique. Cells having plates fabricated according to these procedures have very good high temperature performance and very stable capacity throughout numerous charge-discharge cycles.

The novelty of the AFAPL and Bell processes of impregnation is that precipitation of nickel hydroxide and cadmium hydroxide inside the pores of the plaque is carried out electrochemically from nitrate solutions eliminating the need for conversion through dipping in alkali or through thermal decomposition. These are not the first electrochemical methods of impregnation that have been devised, but they are the only ones reported that can be used for a full loading of plaque without repetitions of the impregnation cycle.[10] Also, with other electrochemical methods it is difficult to deposit the hydroxides inside the pores of the plaque without precipitation in the bulk solution and on the outside of the plaque surface. These side effects result in blockage of the pores limiting the amount of active material that can be introduced into the plaque. In the Bell process these undesirable results are minimized through additon of sodium nitrite to the impregnating bath. In the AFAPL process they are eliminated by use of an ethyl alcohol solution.

Theory of Electrochemical Impregnations

In order to obtain a general understanding of the principles involved in these processes, let us consider what happens to an aqueous

[10] Other methods are reported in the patent literature, but working cells resulting from these have not been reported. See: Pell, M.B., and Blossom, R.W., U.S. Patent 3,507,699 (1970) and Hausman, C.C., U.S. Patent 3,600,227 (1971).

nitrate solution when electric current is passed through it. At the negative electrode (the cathode) nitrate and water are reduced, depending on the applied potential removing hydrogen ions (or producing OH^- ions). Equations representing these half-reactions are shown below. If metal

$$NO_3^- + 2H^+ + e^- = NO_2 + H_2O$$
$$(\text{or } NO_3^- + H_2O + e^- = NO_2 + 2OH^-)$$
$$NO_3^- + 3H^+ + 2e^- = HNO_2 + H_2O$$
$$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$$
$$NO_3^- + 5H^+ + 4e^- = 1/2N_2O + 2\ 1/2H_2O$$
$$NO_3^- + 6H^+ + 5e^- = 1/2N_2 + 3H_2O$$
$$NO_3^- + 7H^+ + 6e^- = NH_2OH + 2H_2O$$
$$NO_3^- + 8H^+ + 7e^- = 1/2N_2H_4 + 3H_2O$$
$$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O$$
$$H^+ + e^- = 1/2H_2$$
$$(\text{or } H_2O + e^- = 1/2H_2 + OH^-)$$

ions, such as Ni^{++} or Cd^{++}, are present that form insoluble hydroxides, they are deposited on the cathode or precipitated in solution as soon as the pH of the solution becomes sufficiently high. In other words, the reaction

$$Ni^{++} (\text{or } Cd^{++}) + 2OH^- = Ni(OH)_2\ (\text{or } Cd(OH)_2)$$

occurs.

At the anode (positive electrode) the reactions occurring depend on the composition of the anode as well as the applied potential. If an inert anode is present, such as platinum, water is oxidized to oxygen and hydrogen ions are generated in solution.[11] If nickel, cadmium, or

[11] If the potential is sufficiently high, platinum can be oxidized.

other oxidizable metal anodes are used, the anodes are eventually consumed into solution. In summary,

$$H_2O \rightleftharpoons 1/2O_2 + 2H^+ + 2e^- \text{ (Inert Anodes)}$$

$$Ni \text{ (or Cd)} \rightleftharpoons Ni^{++} \text{ (or } Cd^{++}) + 2e^- \text{ (Consumable Anodes)}$$

As indicated all the above reactions are reversible. Thus, it is possible to plate nickel or cadmium as metals on the cathode and to oxidize all the various nitrogen compounds back to nitrate. The latter process does occur to some extent under conditions used for electrodeposition of hydroxides in nickel plaques, but plating of metals usually doesn't happen as the potential rarely becomes high enough to allow it.

If ethanol is now added to the nitrate solution, the chemistry becomes much more complex as there are a number of organic compounds formed during electrolysis. In addition, the thermodynamic equilibria controlling the pH or acidity of the solution are changed such that one now has a real problem in trying to characterize the physical as well as chemical aspects of the process. There is enough known about such a system that carrying out electrolysis in aqueous ethanol solutions is not entirely "black magic". The same reactions occur at the cathode as in aqueous media. In addition, reactions such as reduction of the ethanol to ethane are possible.

$$C_2H_5OH + 2H^+ + 2e^- \rightleftharpoons C_2H_6 + H_2O$$

Probably the most significant in terms of plaque impregnation are the anodic reactions concerning oxidation of ethanol to acetaldehyde, acetic acid and carbon dioxide.

$$C_2H_5OH \rightleftharpoons CH_3CHO + 2H^+ + 2e^-$$

$$C_2H_5OH + H_2O \rightleftharpoons CH_3COOH + 4H^+ + 4e^-$$

$$C_2H_5OH + 3H_2O \rightleftharpoons 2CO_2 + 12H^+ + 12e$$

These reactions generate hydrogen ions which neutralize excess hydroxide ions coming from the reduction of nitrates. This effect helps to control the solution acidity and prevents precipitation of hydroxides in the bulk solution.

Lastly, addition of ethanol to an aqueous solution lowers the boiling point. Alcohol and water from an azeotrope[12] at 77° Centigrade. In the presence of nickel nitrate at a concentration favorable for plaque impregnation (Ca. 2 moles per liter) boiling occurs at about 80°C. This temperature permits use of plastic tanks for carrying out depositions and reduces the amount of energy that would be necessary to raise the temperature to the aqueous boiling point of 104°C.

From the above discussion it is readily apparent that there are complicating features associated with competing reactions and the complementary process occurring at the counter electrode. The most important are reactions that tend to change the pH or acidity of the impregnation bath. If the bath acidity is too high, hydrogen ions will remove the hydroxyl ions generated in the plaque pore structure as they can diffuse into the small pores much more readily than nickel or cadmium ions and will reduce the efficiency of the process. If the acidity is too low, deposits will build up on the surface of the plaque

[12] An azeotrope is a boiling solution of two or more liquids whose vapor has a constant composition. The azeotropic temperature is either less than or more than the boiling point of all the constituents. Ethanol and water form an azeotrope which boils at a lower temperature than either constituent having a composition of 95% ethanol.

and deposit in the bulk solution rather than in the pores. In the Bell process inert anodes are used, and hydrogen ion is readily generated. In order to control the increased acidity and buffer the solution, sodium nitrite, which is a weak base and compatible with the chemistry of the bath, is added to the solution. In the AFAPL processes consumable anodes are used and control of the solution acidity does not become as great a problem. Production of hydrogen ion due to oxidation of alcohol is a boon as it does not allow the acidity to become too low. The creation of acetates and acetic acid also probably helps to buffer acidity of the solution. Use of additives to control pH in the impregnation of the negative plate by the AFAPL process is not necessary.

Performance Tests for Improved Cells

Experimental cells having plates fabricated according to the AFAPL procedures show substantial improvement in performance over state-of-the-art cells in terms of cycle life, retention of capacity with cycle life, charge acceptance at elevated temperatures, and energy density. The latter two properties are influenced to some extent by an increased amount of cobalt additive in the positive plate, but mainly by efficient deposition of active material using electrochemical impregnation methods.

When cycled under accelerated failure conditions of elevated temperature, moderately high charge and discharge rates (one hour charge/one hour discharge) and 100% depth of discharge, 22 ampere-hour AFAPL cells underwent over 750 charge/discharge cycles. Under the same conditions state-of-the-art aircraft cells of the same rating failed between 500 and 650 cycles.

The improved retention of capacity with cycle life for AFAPL cells is illustrated in Figure 1. The fading of capacity with cycle life in nickel-cadmium cells is caused by the negative plate, apparently because the small particles of active material tend to agglomerate reducing the active surface area of the plate. This effect is more pronounced with metal electrodes. It is apparently minimized, or at least greatly reduced, by efficient distribution of the active material throughout the plate with an electrochemical impregnation. The results shown in Figure 1 were taken from negative limited three plate cells all having equal electrode volume. Capacity per pound is 50 ampere-hours for the E.I. electrode as opposed to 40 ampere-hours for the electrode in cell A and 46 ampere-hours for the electrode in cell B. Electrodes for A and B were taken from unused standard aircraft cells. The cells were charged and discharged at the one hour rate. Although a small number of cycles were recorded, one can readily tell that the trend of the curves for cells A and B is toward a more rapid decrease in capacity than for the AFAPL cell.

The difference in capacity density (or energy density) is much more pronounced in the positive AFAPL electrodes when compared to commercial. Performance of AFAPL positive electrodes produced at a beaker level are shown in Table I. Capacities are given in ampere-hours. When cycled under the same conditions state-of-the-art aircraft electrodes have a capacity of about 5 to 6 ampere-hours per cubic inch. If cycled further, the AFAPL electrodes exhibit about 120% utilization of active material.[13]

[13] The reason for percent utilization being over 100 is that theoretical capacity is based on a <u>one</u> - electron change, i.e., on the reaction

$$NiOOH + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$$

The above reaction is oversimplified. An explanation has been offered recently. See: J.F. Jackovitz and D.W. Feldman, Extended Abstracts Publication of the 1972 Spring Meeting of the Electrochemical Society, Miami Beach, Fla., 1972, Abstract 25, p. 67.

Ironically, on scaling the process up to production better results were obtained. Results of the first and fourth impregnation are shown in Table II. Assuming 120% utilization of active material can be obtained from these electrodes, they should have a capacity of greater than 10 ampere-hours per cubic inch.

The apparatus used for impregnation is shown in Figure 2. It consists of five anodes and four 9 1/2 inch by 8 1/4 plaque cathodes. Each plaque is coined into six 2 3/4 inch by 4 3/4 inch electrodes. The bath is contained in the polypropylene tank and heated by circulation through an external resistance heater.

Plates from plaque numbers SU-1 through SU-4 have been combined with negative plates made from a similar impregnation apparatus. The resulting cells have been cycled at elevated temperatures and their charge efficiency versus state of charge curves recorded. A comparison of this data with data recorded for standard 22 ampere-hour aircraft cells under the same conditions is shown in Figure 3.

From these results it can be seen that a much more efficient battery results from the electrochemically impregnated plates. For example, at 130°F[14], a maximum of 71% of the total capacity can be obtained from an aircraft battery, and this is with an overcharge of about 40%. At the same temperature better than 85% of the capacity can be obtained with the AFAPL cell with less than half the amount of overcharge. At 90°F the AFAPL cells are far superior to the aircraft cells at 75°, and at 110°F there is hardly a comparison between the two.

[14] This could be the temperature of a battery in an aircraft taxiing on a runway in the Southwest during summer.

These results are also partly due to high concentrations of cobalt hydroxide in the active material (Ca. 10 mole %). It has long been known that cobalt improves high temperature charge acceptance in the nickel hydroxide electrode along with capacity and cycle life.[15]

Recent work by Maloy[16] in our laboratory has offered a partial explanation for this effect. Using cyclic voltametric studies it was revealed that presence of cobalt hydroxide increases the reversibility of electron transfer in the charge-discharge cycle; in the absence of cobalt hydroxide a difference of 150 mV is observed between charge and discharge peak potentials. In the presence of Ca. 10% cobalt hydroxide, this difference is only 75 mV. The cyclic voltametric curves are shown in Figure 4.

Chronocoulometric studies of Maloy[16] show that, in presence of cobalt hydroxide, charge efficiency was 30% greater for the micro electrode that was used, at room temperature. High temperature studies were not attempted.

The effect of moderately high temperature cycling (90°F) has been studied by Lander and Pickett using pilot plant fabricated electrodes with the same amount of cobalt.[17] Cells tested yielded greater than 90% of original capacity at over 1700 charge-discharge cycles at the one-hour rate of charge and discharge. Charging efficiency was also greater than 98% at 85% of measured capacity.

15 S.U. Falk and A.J. Salkind, Op. Cit., p54.

16 J.T. Maloy, "The Effect of Cobalt Hydroxide Coprecipitation in Nickel Hudroxide Electrodes", Final Report under 1975 ASEE-USAF Summer Faculty Research Program, August, 1975.

17 J.J. Lander and D.F. Pickett, Paper submitted for presentation at 27th Power Sources Conference, June, 1976, Atlantic City, N.J.

Under contract with Spectrolab AFAPL type electrochemically impregnated electrodes were used in fabrication of space cells. These cells are presently under test at the Naval Weapons Support Center, Crane, Indiana. Initial tests by Spectrolab showed capacities greater than 20 watt-hours per pound (versus 16 W-hr/lb for state-of-the-art).[18]

The nickel hydroxide electrode made by electrochemical impregnation processes appears to be a natural candidate for the new nickel hydrogen cell due to its structural stability with respect to cycle life. Swelling of nickel hydroxide electrodes forces electrolyte out of the separator, thus drying out the cell stack. Also, the more demanding heat removal problems of the nickel hydrogen cell sometimes forces cell designers to use very narrow distances between the cell stack and cell container. If an electrode is used which is not structurally sound, the plates can be shorted by the metal container.

Recent tests in our laboratory have shown that the AFAPL nickel hydroxide electrode can withstand over 400 room temperature charge-discharge cycles at deep depths of discharge without any change in dimensions.[19]

In addition to results presented here tests have been performed by TRW Systems Group which strongly favor the use of these electrodes in aerospace nickel-cadmium and nickel hydrogen cells.[20] Work is continuing on these processes and plans are being made for manufacturing development in the very near future.

[18] V.J. Puglisi and E.L. Ralph, "Development of Nickel Alkaline Batteries for Aerospace Lightweight Secondary Power", Final Report under Contract F33615-73-C-2012; AFAPL-TR-75-64, June, 1975.

[19] D.F. Pickett, et al. Paper submitted for presentation at the 27th Power Sources Conference, June 1975, Atlantic City, N.J.

[20] R.H. Sparks, P.F. Ritterman and R.E. Patterson, Unpublished results.

TABLE I

PERFORMANCE OF NICKEL HYDROXIDE ELECTRODES
IMPREGNATED FROM ETHANOL SOLUTIONS

Plaque #	Theo.* Capacity	Measured# Capacity	% Utilization& of Active Matl.	A-H per cc of Void	A-h per in^3	Thickness (20 Cycles)
1	1.648	1.399	84.9	8.90	7.28	0.0261
2	1.968	2.208	112.2	10.10	8.19	0.0370
3	2.066	2.020	97.8	9.14	7.42	0.0347
4	2.032	2.020	99.4	9.17	7.44	0.0344
5	1.973	2.020	102.4	9.55	7.75	0.0328
6	1.973	2.020	102.4	9.64	7.81	0.0330

*--Assuming weight gain due to $Ni(OH)_2$ + $Co(OH)_2$, and $Co(OH)_2$ is active material.

#--2.5 amp. charge to 120% of theo. capacity then discharge at 2.5 amps. to 0.9 volts. Average of cell with 3, 4, 5, and 6 taken.

&--After 20 charge/discharge cycles.

TABLE II

SCALE-UP LOADING CHARACTERISTICS OF NICKEL HYDROXIDE ELECTRODES IMPREGNATED FROM ETHANOL SOLUTIONS

(9.50" x 8.25" x 0.030" plaques including six 2.75" x 4.75" electrode areas with .20" coining between areas, 0.100 around edges)

Plaque #	Wt. of Active Matl.	Wt. of Matl. per cc void*	Theo. Capacity	Thickness gain on Impreg(in)	Theo. Ah/in^3
SU-1	58.80	1.73	16.99	.0016	7.0
-2	57.60	1.70	16.64	.0028	6.7
-3	58.40	1.72	16.88	.0031	6.8
-4	59.00	1.74	17.05	.0026	6.9
-13	77.50	2.29	22.40	.0036	9.0
-14	75.85	2.24	21.92	.0025	8.8
-15	77.60	2.29	22.47	.0036	9.0
-16	78.45	2.31	22.67	.0040	9.3

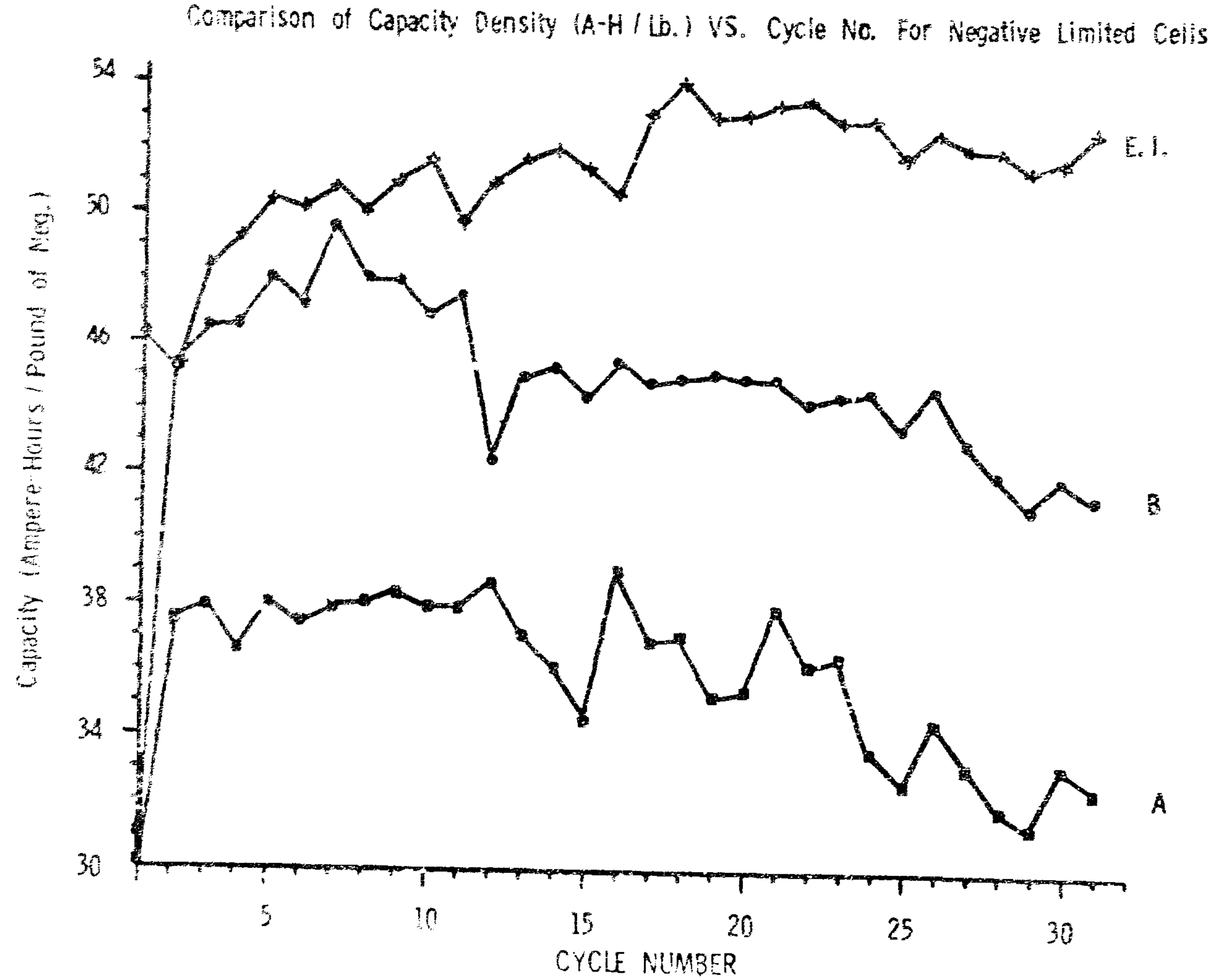


Figure 1. Comparison of Capacity Vs Cycle No. for Commercial and AFAPL Cadmium Electrodes

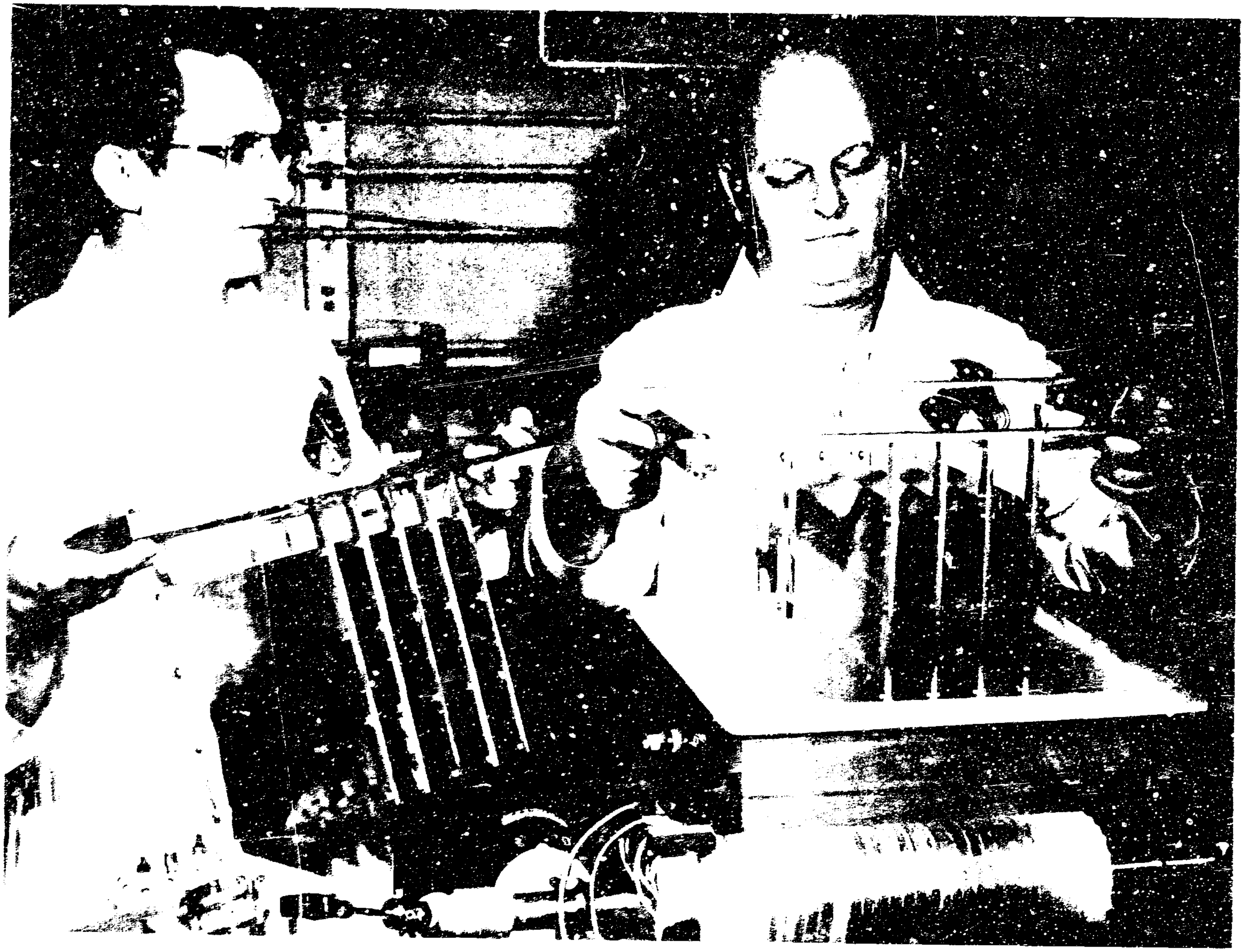


Figure 2. Impregnation Apparatus

CHARGE EFFICIENCY VS STATE OF CHARGE

AIRCRAFT CELLS ______

AFAPL CELLS ....

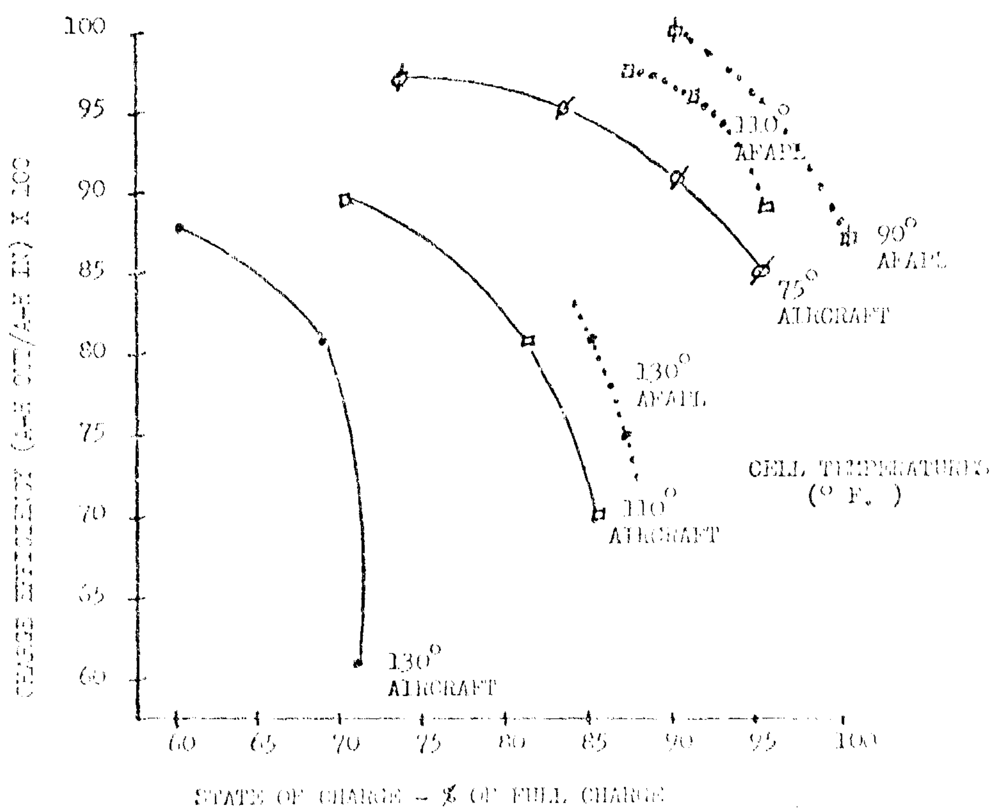


Figure 3. Comparison of Charging Efficiencies for AFAPL and Aircraft Cells

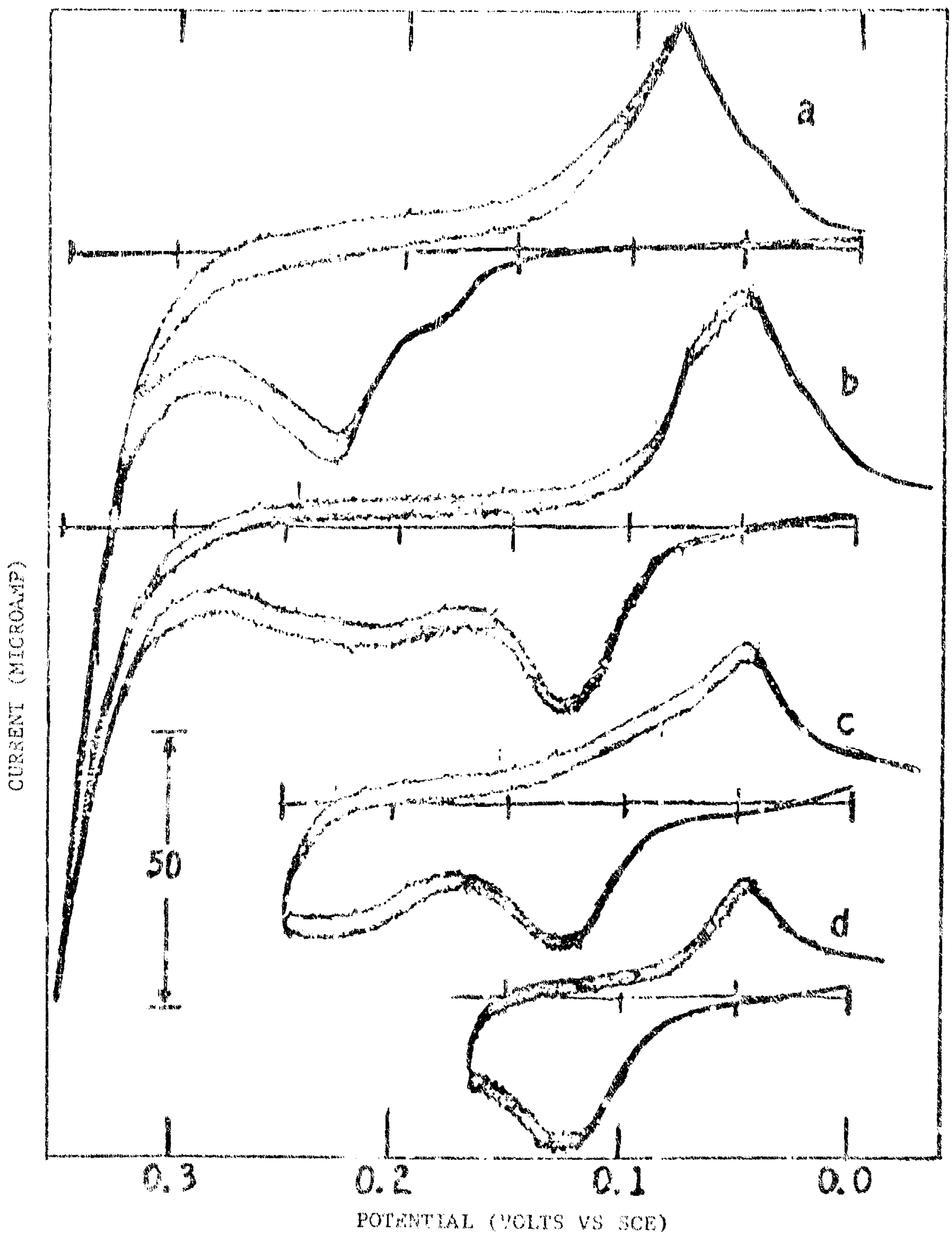


Figure 4. Slow Scan Cyclic Voltametry of 30% KOH Solutions at the Nickel Hydroxide Electrode
a. No $Co(OH)_2$; b., c., d., 10% $Co(OH)_2$

DRY CHARGED NICKEL OXIDE ELECTRODES FOR RESERVE NICKEL OXIDE-ZINC BATTERIES

Nickel oxide-zinc batteries are presently being investigated as alternates to the more costly silver oxide-zinc batteries currently used in a number of applications. Because of the long stand times involved in some cases, a reserve battery, in which the electrolyte is stored separately for the cell stack, must be used. The electrolyte is injected into the cell chamber in order to activate the battery. For such a system to be feasible, dry charged electrodes having stand times on the order of several years are required. The positive electrode is almost always the limiting factor in this case as it has a relatively unstable oxide as active material. For example, Ag_2O_2 is unstable except in alkaline solution, and Ag_2O is not stable at high temperature (>300°C). For the system under investigation, the unstable oxide is nickel (III) oxide or nickel (III) hydroxide. Techniques for making stable nickel oxide electrodes have been investigated in our laboratory as well as in other organizations. There is data, of a proprietary nature, suggesting that it is quite possible to construct a reserve nickel-zinc battery with several years stand life.

One technique which has been demonstrated in our laboratory involves charging conventional vacuum impregnated plates in KOH electrolyte then washing in distilled or deionized water. The plates are then vacuum dried in a dessicator or stored under vacuum for 16 to 72 hours. The plates yield rated capacity upon activation. Results of some tests are shown in Figure 5. No long term dry storage data is available on this technique as yet. It appears that this method would be applicable to plates made by other processes

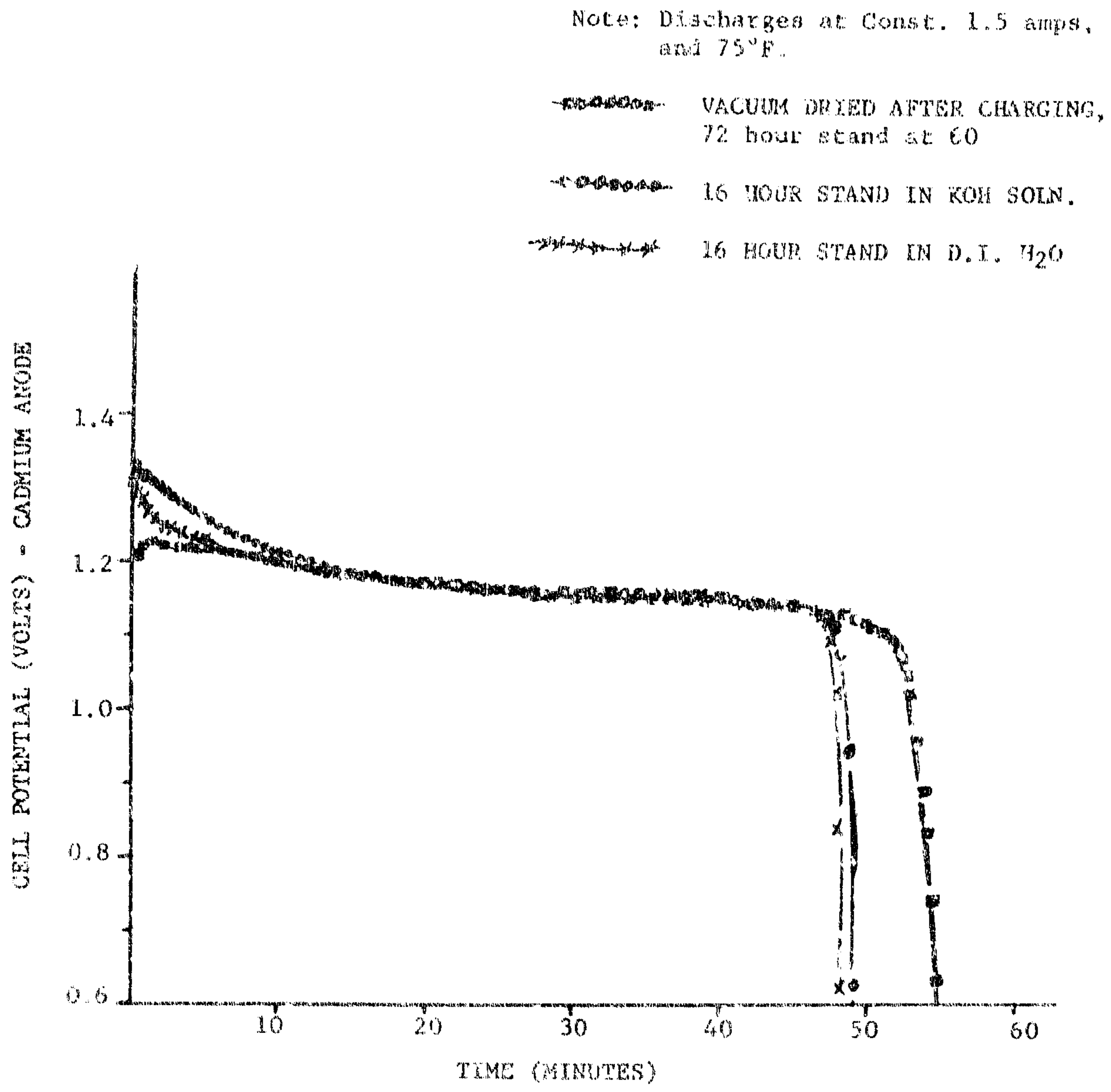


Figure 5. Discharge Curves for Wet and Dry Stand Nickel Hydroxide Electrodes

SILVER OXIDE-ZINC ELECTRODES FOR A MULTICELL PILE TYPE HIGH POWER BATTERY

Investigations into the feasibility of a secondary pile type silver oxide-zinc battery as a candidate for use in a megawatt level power system was initiated in July 1973 by Eagle-Picher Industries under USAF Contract Number F33615-73-C-2074. The objective of this nine month program was to demonstrate the capability of individual components under the environmental and electrical conditions required for such an application and project an overall system design. Results of the above program led to the initiation of the second phase of the program by Eagle-Picher Industries under USAF Contract Number F33615-74-C-2045. The objective of this present program is to develop and build the basic system building block which is a 100 kilowatt (500 volts and 200 amps) module.

The present status of the program includes the final optimization of the basic cell components and their interactions, and testing of full scale multicell piles to verify the designs.

The general design of the battery system is modular in nature so that the system can fit the application. Figure 6 is a graphical representation of the design of a battery system. Stacks of approximately forty cells are constructed into a submodule of 50 volt and 200 amp capability. Ten submodules then make up a module with the addition of end plates (which house electrical components and interlocking guide rails) and restraining rails. A system is then configured by interlocking (physically and electrically) modules.

At the heart of the submodule is the pile type cell shown in Figure 7 and the most unique characteristic of the cell is the bipolar electrode which consists on an intercell connector, a cathode and the anode for the adjacent cell.

The intercell connector for the bipolar electrode serves as the cell case, active material substrate, and the electrical connection between individual cells in a pile type battery. The intercell connector minimizes the electrical resistivity from cell-to-cell resulting in a considerable reduction in voltage losses, and since the connector serves as a common substrate to anodes and cathodes, the current is distributed evenly across its surface, which should lend itself to retarding "shape change" of the anode.

Studies pertaining to the intercell connector have been directed toward: surface preparation, compatibility with the electrochemical system, and overall mechanical and electrical properties Silver has been the primary material utilized in these studies and is procured per MIL-S-13282A in a continuous roll twelve (12) inches wide. Preparation of the foil surface was directed toward producing a rough surface for attaching the active materials, both silver and zinc. Processes which were evaluated included: sandblasting, acid etch, and electrochemical etch, with electrochemical etching in potassium cyanide found most favorable.

In the studies of the negative electrode it was found desirable to protect the silver foil on the negative side from the common electrolyte. To achieve this approach, one side of the silver foil has been electroplated with a thin uniform layer of zinc. The electroplated zinc on silver foil as the anode side of the intercell connector appears superior and the reason will be discussed later.

The positive side of the bipolar electrode has caused fewer problems than any of the individual components in development of the pile battery, and the processing equipment was also the least problem to set up. During the feasibility study the most promising cell configuration included the use of an uncharged positive electrode, which also simplifies the process by eliminating its electroformation prior to cell fabrication.

The present configuration of the positive electrode is a sintered, porous silver matrix as shown by SEM photographs of Figure 8. This material is deposited onto the cathode side of the intercell connector which has been prepared as described above. The active material distribution is controlled from .12 to .15 grams per square inch at a thickness of .0016 inch.

The active positive material is sprayed over the entire surface of the silver foil extending across the seal area.

Processing of the positive side of the bipolar electrode has been set up in such a manner that it can be used in a continuous line. However, since only a limited number of electrodes are required for this phase of the contract, the equipment is used as a piece part setup. The processing equipment is divided into three (3) separate sections, each designed for continuous operation. They are:

1. Spray deposition
2. Drying/Sintering
3. Pressing

The present process rate is approximately 100 electrodes per hour with continuous potential of 600.

The spraying operation consists of a vented spray booth with a conventional paint spray head mounted over a continuous belt. The spray head is microswitch activated as the continuous belt feeds single electrode foil positioned on a rack. The rack is fabricated from woven nickel screen allowing overspray to go through without damaging the sprayed foil by over or under running.

The drying/sintering oven is constructed from infrared heating modules with the first seven (7) modules adjustable so that the temperature is limited to approximately 300°F providing a zone for drying The sintering is performed in the next zone of 4 modules where the temperature reaches approximately 900°F.

Pressing of the electrodes is performed by two (2) four (4) inch diameter rollers. The bottom roller is permanent while the top floats under a controllable pressure.

Considering all components of the pile battery design, most of the problems, during this contract, have occurred in the configuration and processing of the negative electrode. Since the design of the pile battery is more desirable as a dry-uncharged unit, it is necessary that the negative electrode contain, as a minimum, sufficient zinc oxide to charge the positive electrode initially. The remainder of the active material is most desirable as zinc, and more adaptable to thin film electrode processing.

The present configuration of the negative electrode consists of vapor depositing onto the intercell connector, a porous zinc structure. Figure 9 shows the physical structure of vapor deposited zinc by SEM photographs. The intercell connector used for the zinc deposition has previously been processed for the positive, with the exposed negative side prepared as described earlier. The active material is deposited directly onto the intercell connector at a material distribution of .12 to .14 grams per square inch with a density of 55 to 56 grams per cubic inch. The zinc is applied only to the active cell area, leaving a foil edge to which the seal is attached. Chemical analysis of the vapor deposited material has been shown to be 99.4 percent zinc. A final coat of zinc oxide is applied to complete the electrode by spraying the active material with .06 grams/inch^2 of zinc oxide.

The electrode described in the preceding paragraph has culminated in a structurally and electrically proven electrode resulting in its use in test cells and piles. Problems have been evident and are contributed mainly to internally generated gases which when compounded with the overall physical configuration, prevents the maximum from being exhibited by the negative electrode.

Processing of the negative electrode side of the bipolar electrode is set up on a batch basis. The present capability can produce 16 electrodes in two (2) hours which is limited by the physical size of the vacuum chamber. Full production could be scaled up either in a batch basis or as a continuous strip. To produce 100 electrodes in a batch process would require a chamber approximately six (6) feet in diameter by six (6) feet long.

Difficulties were encountered when the negative electrode was applied directly on silver foil. Because of the physical structure of the negative material (porous down to the silver foil) when electrolyte came in contact with the silver-zinc junctions effectively a shorted couple was produced. This problem caused severe gassing on activation and these gasses were not being effectively removed. To alleviate this problem, beaker type tests are being conducted on electrolyte additives and bimetal intercell connectors. Results of these tests have shown that by adding ZnO to the electrolyte (saturated) and using the intercell connector discussed earlier with electroplated zinc against the silver foil (this eliminates the common electrolyte) the activation gasses can be reduced substantially.

The physical design is modular in nature so that the system configuration is dictated by the application. The basic system building block is a 100 kw module as shown in Figure 10, which contains ten (10) fifty (50) volt submodules. The end plates serve the dual purpose of housing the module electrical components and in conjunction with the side rails form the physical restraining system for the submodules. The end plates will have male and female interlocking straps so that the positive end plate of one (1) module will mechanically interlock with the negative end plate of another module.

Two (2) areas are being examined independently in the design of the module electrical system. First, the monitoring system will functionally be split into charge and discharge systems and the requirements for each have been examined. Second, the control system which must be capable of handling discharge currents of 200 amps has been considered. Figure 11 is functional block diagram of a module electrical system, including monitoring and controls. It is felt that this system would be the minimum system required.

Data collected during this contract has been used in a projection program to calculate the weight and volume characteristics of a complete module and system. As a base power level, a module of 100 kw was used for the projection to a four (4) megawatt system. These projections include packaging and system electrical interconnection.

Figure 12 shows a comparison at various module power levels for the combinations shown. The first design is a projection using existing test data from multi-cell tests and shows physical capabilities in comparison to that projected. The results are within approximately 10% and are exceptionally close considering that the test cells were not purposely held to physical minimum such as the seal and sump design.

The electrical performance of full scale ten cell piles is shown in Figure 13. A current density of 2.0 amps/in^2 appears to be the upper limit when considering end voltage and a current density of 1.3 amps/in^2 is the lower limit due to module weight and volume.

The primary problem encountered with the full scale piles was cycle life which is attributed to the internally generated gasses discussed earlier and an inadequate means of removing those gasses. However, Figure 14 is a graph of cell power versus cycles and it shows that single cell piles cycled as high as fifty cycles (solid lines) and the components have demonstrated better than eighty cycles (dashed line) in beaker type tests. It is felt that with the improvements discussed earlier, cycle life requirements can be satisfied.[21]

[21] - This section of the report was taken from AFAPL-TR-75-51, "High Rate, Rechargeable, Silver-Zinc Pile Type Battery", May 1975, by L.R. Erisman. It is the final report under Contract F33615-74-C-2045 and has limited distribution to U.S. Government agencies only. Mr. Marsh initiated this contract work. The information extracted here by Mr. Marsh has unlimited distribution.

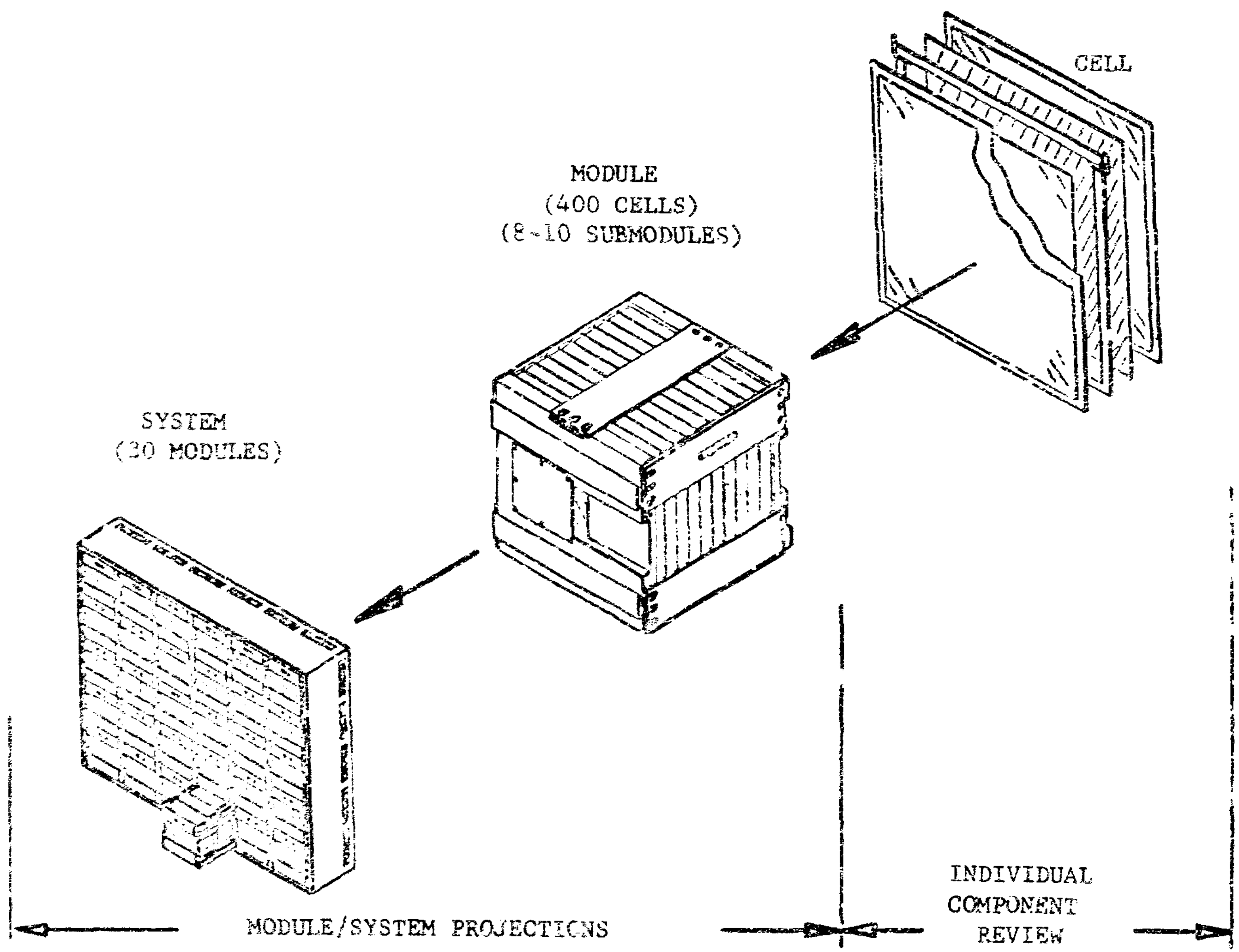


Figure 6. Module/System Physical Breakdowns

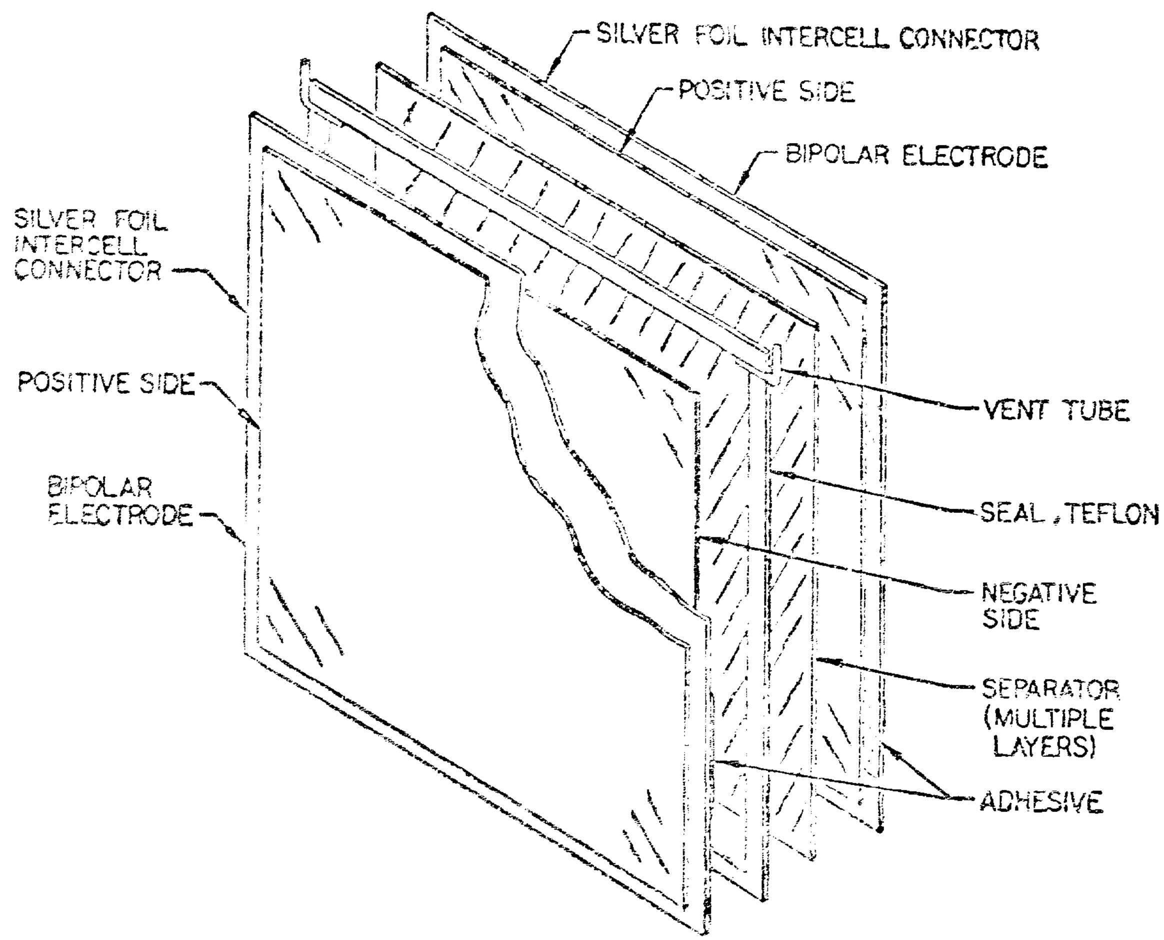
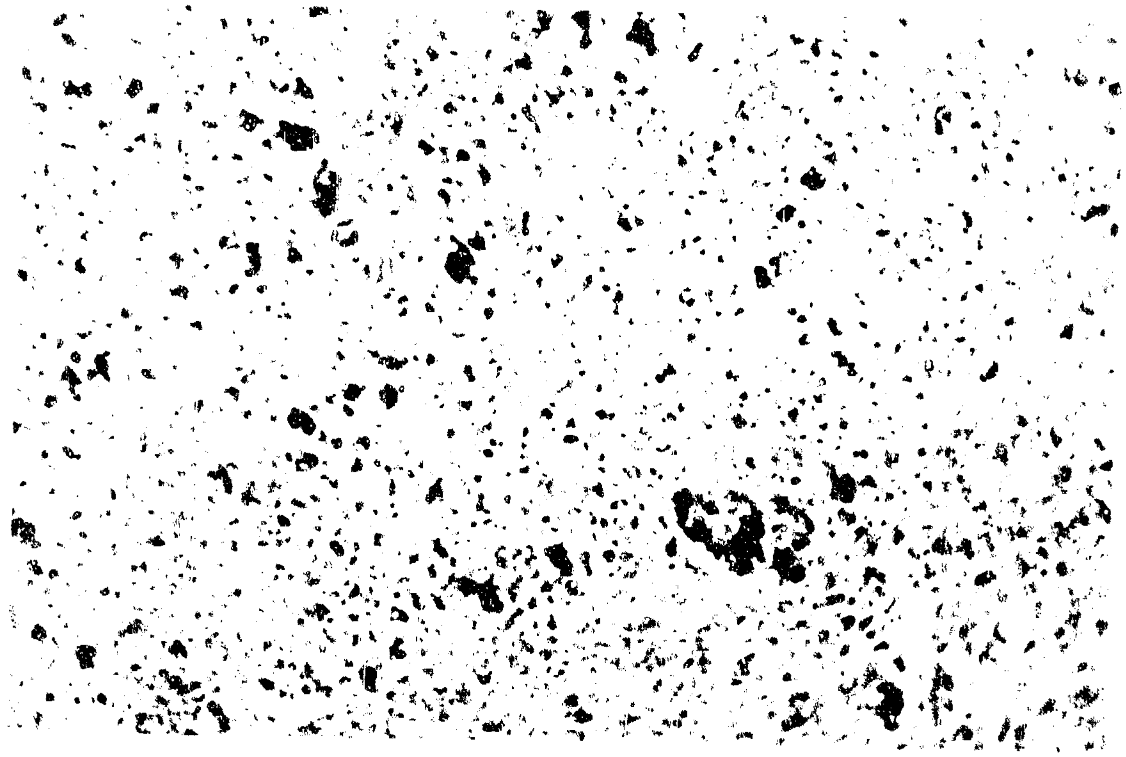
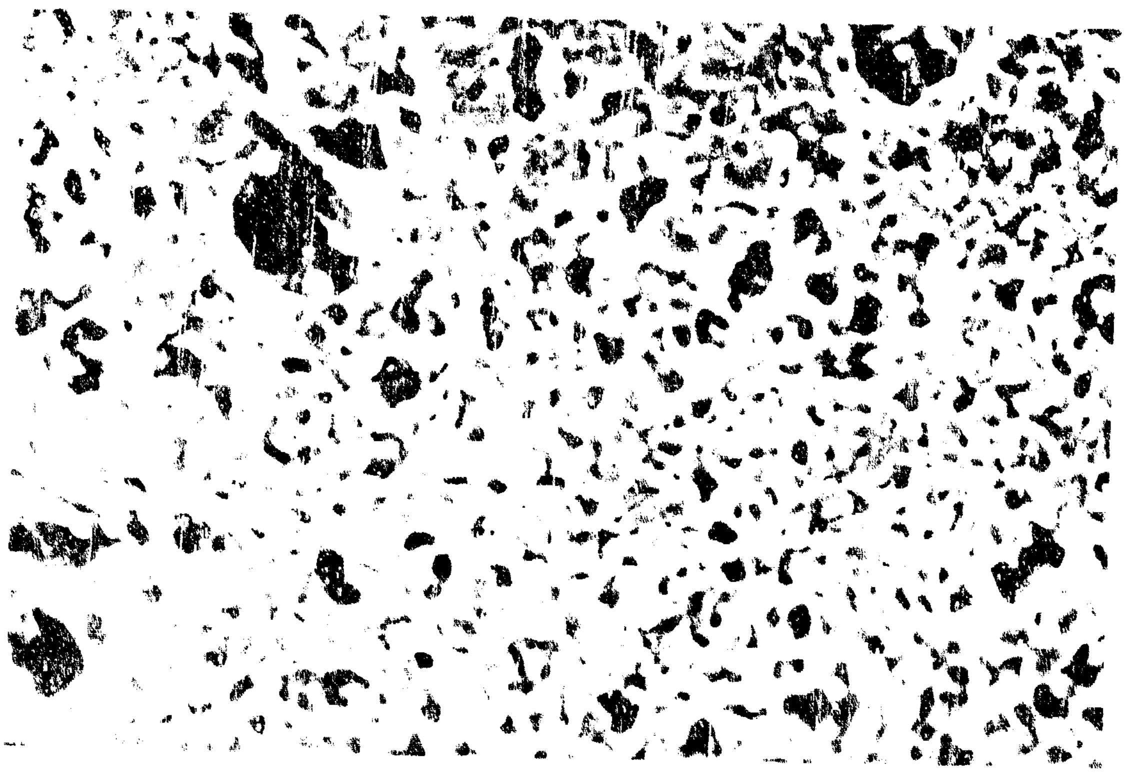


Figure 7. Relationship of Components



300X



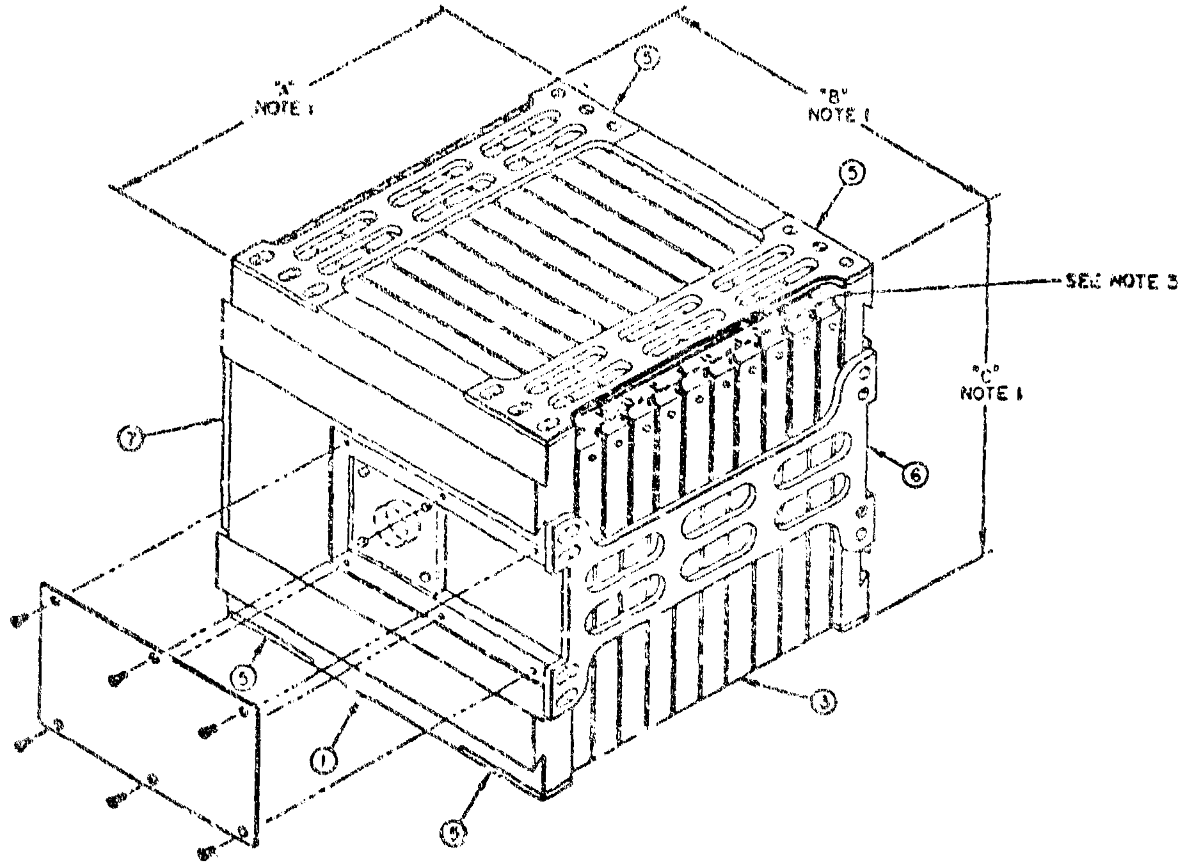
1000X

Figure 8. Positive Electrode Surface, 300X and 1000X

300X

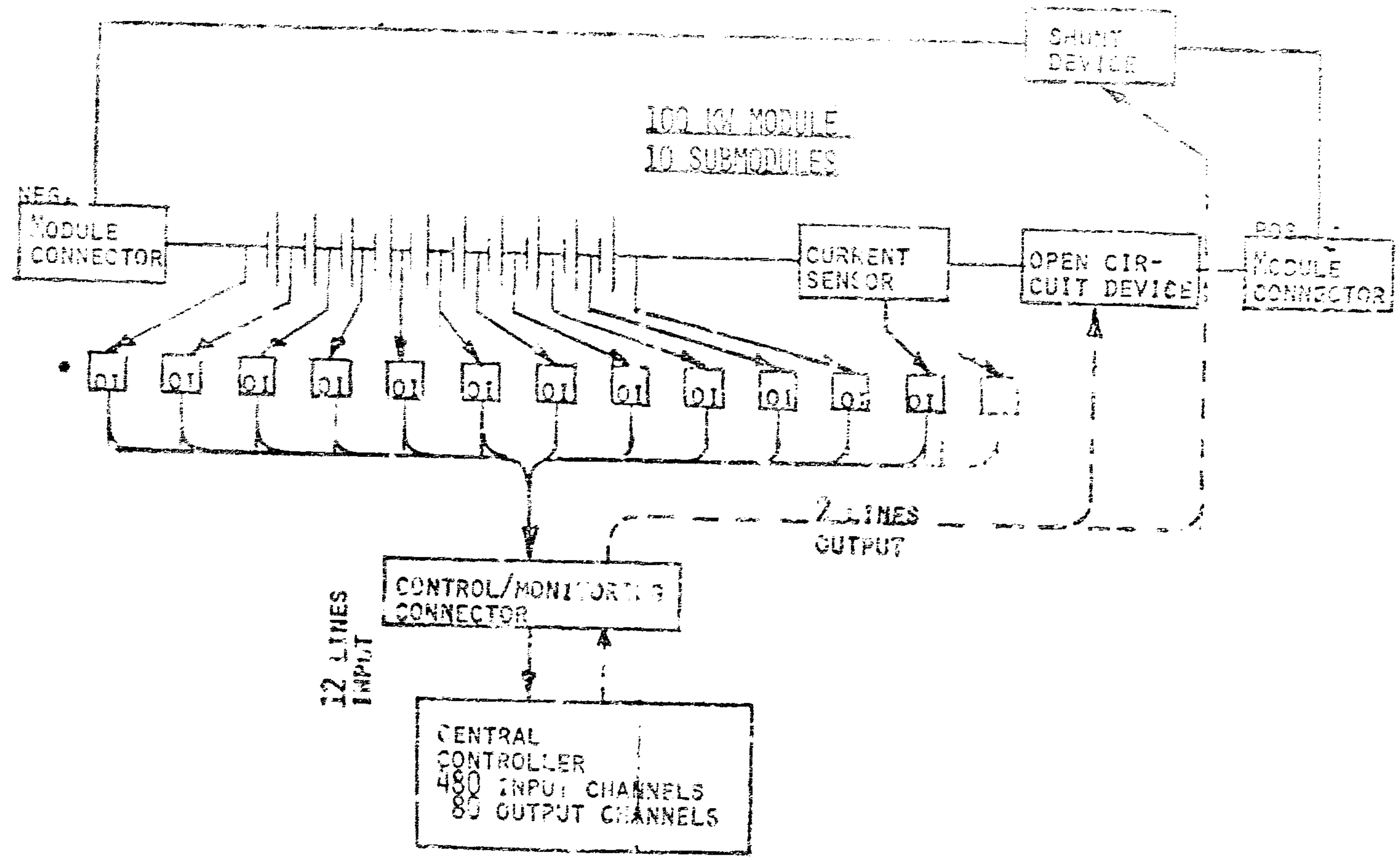
1000X

Figure 9. Negative Electrode, 300X and 1000X



NOTES:
1. Reference MWPP
2. Dimensions A, B, & C to be determined by Subschedule Dimen.
3. Cover caps not shown but required. See parts list for details.

Figure 10. 100 KW Module



*NOTE: O.I. - OPTICAL ISOLATION

Figure 11. Module Monitoring/Control System

(TABLE III)

SYSTEM WEIGHT AND VOLUME PROJECTIONS
FOUR (4) MEGAWATT
1.75 AMPS/IN2-30 SECOND DISCHARGE

	MODULE POWER		
	100 KW WT/VOL	200 KW WT/VOL	500 KW WT/VOL
1. TEST DATA PROJECTIONS	4076/30.6	3833/27.3	3687/25.3
2. REFINED DESIGN (MEDIAN RANGE ZN)	3816/26.4	3573/23.0	3289/19.8
3. SEPARATOR IMPROVEMENT	3648/25.1	3405/21.8	3259/19.8
4. INTERCELL CONNECTOR (AG/ZN LAMINATE)	3684/26.4	3441/23.1	3295/21.1
5. COMPOSIT (PROJECTION 2, 3 AND 4)	3517/25.1	3273/21.8	3127/19.8
6. ZN IMPROVEMENT (HIGH RANGE)	760/26.1	3517/22.8	3371/20.8
7. COMPOSIT 5 AND 6	3444/24.8	3201/21.5	3055/19.5
8. TWO (2) MINUTE DISCHARGE			
REFINED DESIGN	6435/37.5	6192/34.2	5907/31.0
COMPOSIT 5	6136/36.2	5892/32.9	5747/31.
COMPOSIT 7	5846/34.8	5602/31.5	5457/29.6

Figure 12

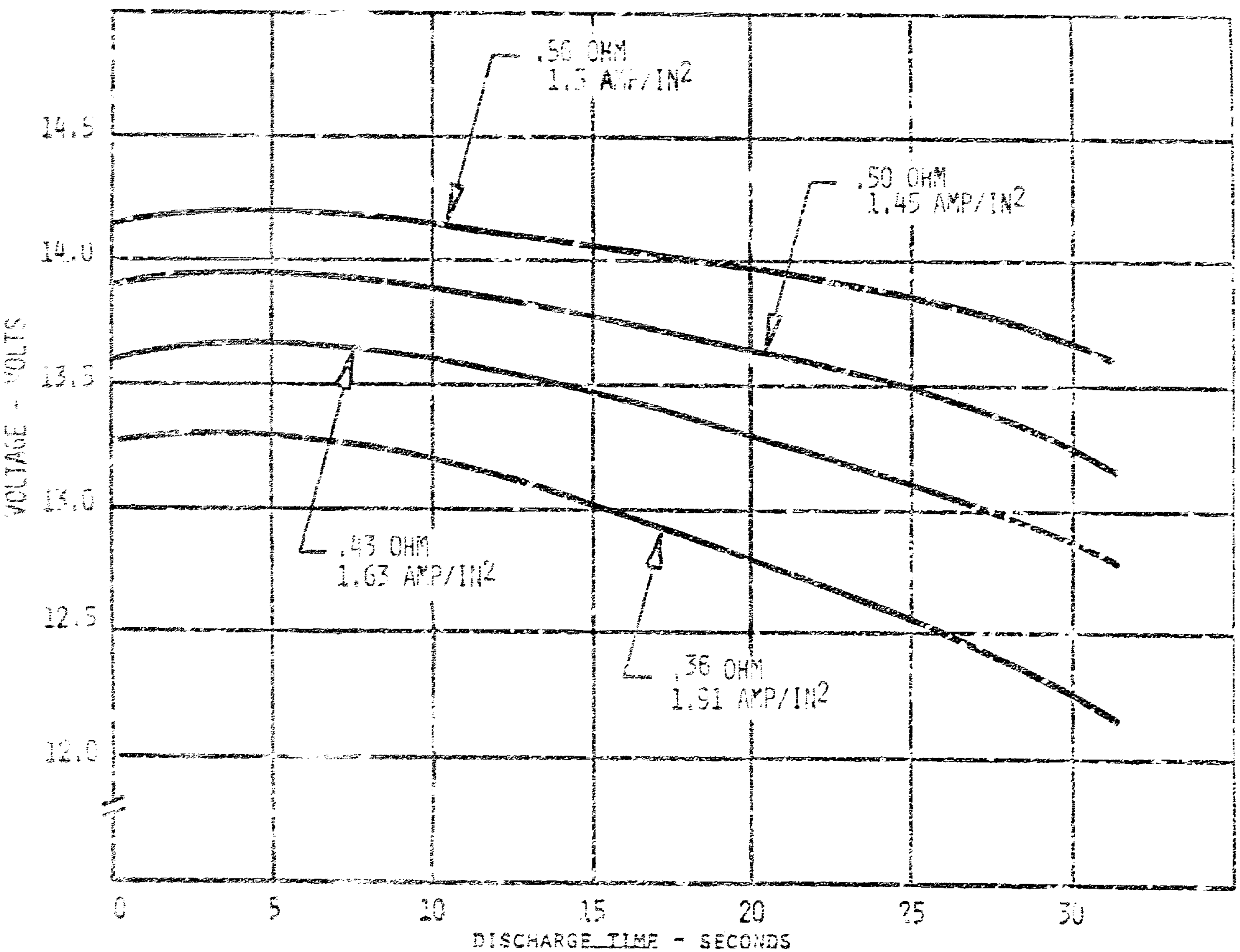


Figure 13. Discharge Curves - Ten Cell Pile

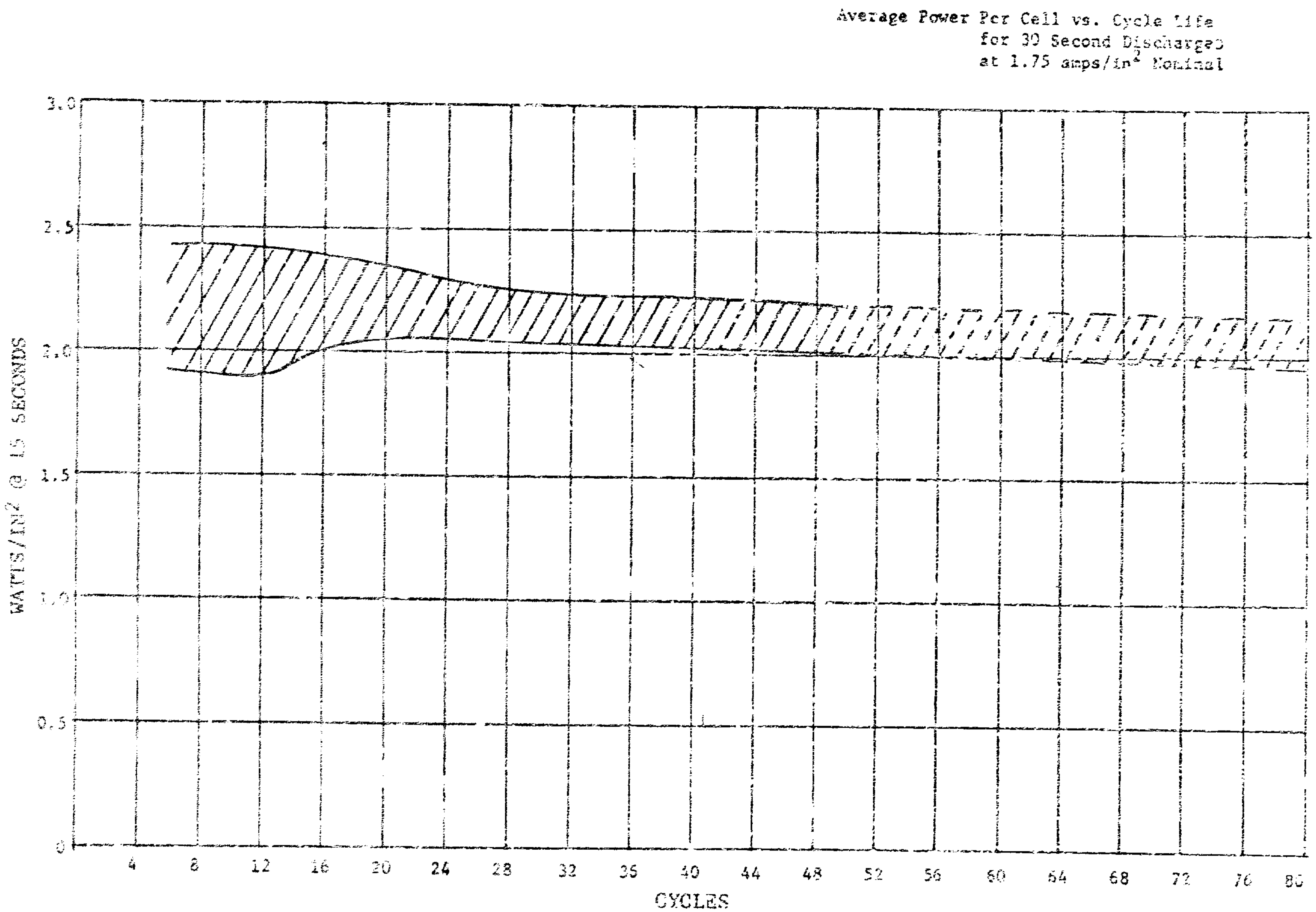


Figure 14. Cell Cycle Life Data

CONCLUSIONS

From results presented here it is shown that significant advances in alkaline battery electrode development are being made. These advances are not only applicable to military uses, but a number of spin-offs on the commercial market appear to be feasible. For example, the new nickel cadmium electrodes can be used both in the Commercial Satellite and aircraft industries. The reserve batteries could be used for a number of emergency power applications. Possibly, the pile type battery could be used for portable tools, if the cost could be attractively reduced.

In short, advances such as these are necessary for our national defense, and may have spin-offs to the commercial market.