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Final Report

DEVELOPMENT OF UNIFORM AND PREDICTABLE BATTERY MATERIALS FOR NICKEL-CADMIUM AEROSPACE CELLS

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ABSTRACT

The objective of this contract was to study and analyze battery materials and manufacturing methods with the aim of developing uniform and predictable battery plates for nickel cadmium aerospace cells.

The experimental approach involved:

1. The preparation of porous nickel plaque and the measurement of its physical characteristics to test for uniformity.
2. The impregnation of the porous plaque with nickel or cadmium hydroxide to form positive and negative plates.
3. The testing and characterization of the plates to define the influence of manufacturing and operating variables.

The results of the first two tasks were discussed in previous reports, and only a short description of the major findings is presented here.

This report presents the results of an extensive factorially-designed experiment aimed at illuminating, in a comparative study, the effect of plaque preparation, plaque thickness, impregnation process, and loading level with active material. The following impregnation processes were investigated: (1) chemical conversion, (2) electrochemical conversion, and (3) high temperature electrochemical impregnation. The test parameter on which the conclusion regarding the manufacturing variables are based was the capacity change during a simulated near-earth orbit cycle regime. As operational variables, the effect of various charge and discharge rates was investigated.

During the 100 test cycles, overall capacity changes of positive plates and the differences between the various plates were found to be small. Plates prepared by the high temperature electrochemical impregnation of slurry-coated plaque (at the conditions used) showed surface buildup of active material. They also retained slightly less of their capacity during cycling compared to other plate preparations. It appears not justified, however, to attribute this difference to the impregnation process as such since it is strongly dependent on the proper plaque structure. Positive electrodes cycled between 75 and 100% state-of-charge at the beginning and approximately between 35 and 60% state-of-charge at the end of the test

period. The plate potential changed significantly during the regular discharge cycle (~ 150 mV). Characteristic memory effects were observed in potential-time curves. The physical integrity of the plates was good. Only the loose-sintered plaque, highly loaded with active material by the chemical conversion method, showed a substantial weakening of the plaque structure due to corrosion.

The test cycling of negative plates resulted in larger overall capacity changes and in larger differences between the various electrode preparations. The highest capacity retention was obtained with plates prepared by the high temperature electrochemical impregnation process. The superior performance of this impregnation technique may result from a more uniform deposition of the active material in the plaque structure. Plaque type and loading were also of importance with the slurry-coated plaques (lower porosity) and the lower loading levels showing the smaller fractional change in capacity. Significant interactions were observed between the various parameters. Negative plates showed no memory effects. The physical properties and the appearance of all plates was very good.

The effect of various charge and discharge rates covering a full order of magnitude was investigated for a selected group of differently-prepared positive and negative plates. The highest delivered capacities of positive plates were obtained at high charge and low discharge rates. The charge and discharge effects were approximately 5% of the average capacity. With the various positive electrode preparations, only small differences were observed regarding the effect of charge and discharge rate on capacity. Negative electrodes delivered higher capacities at low charge and discharge rates. Again, the differences between the various preparation were small. The charge and discharge effects were approximately 6 and 13% of the average capacity, respectively.

The charge and discharge potentials for positive and negative plates showed distinct differences for the various preparations. They were more pronounced for negative plates. The smallest polarization of negatives was observed with slurry-coated plaques impregnated by the high temperature electrochemical process. Plates highly loaded by chemical conversion showed the highest polarization on charge and discharge.

Based on the results of this investigation, acceptable positive plates may be obtained by any of the three impregnation processes on any of the plaques investigated. Negative plates prepared by the high temperature electrochemical impregnation process show a significantly more favorable capacity retention than those prepared by either of the two conversion processes.

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I. INTRODUCTION

The development of more reliable nickel cadmium batteries for aerospace application is dependent on improvements in the uniformity and reproducibility of battery components and great care in the design and assembly of cells. This program was aimed at the first of these objectives: the preparation and identification of uniform battery plates.

1. The preparation of porous nickel plaque and the measurement of its physical characteristics to test for uniformity.

2. The impregnation of the porous plaque with nickel or cadmium hydroxide to form positive and negative plates.

3. The testing and characterization of the plates to define the conditions under which uniform behavior could be achieved.

Prior to the commencement of the experimental aspects of this program, a survey of the current practices in nickel cadmium battery manufacture was carried out. The survey was based on the open literature and discussions with several of the major manufacturers in the United States and was the subject of the First Quarterly Report on this contract.[1]

The first phase (described in earlier reports)[2] emphasized: (1) the production of uniform porous nickel plaque from both loose sintering and a slurry coating process, and (2) the development of experimental techniques to identify uniform physical characteristics.

In the experimental program, the uniformity of the raw materials — INCO types 255 and 287 carbonyl nickel powder — was established as a prelude to plaque fabrications. Fourteen batches of these powders, which are exclusively used in battery plaque manufacture, were examined. In addition, two batches were examined in detail to check variability within a batch. The physical measurements made were bulk density (by Scott volumeter), surface area (BET method using Kr), the Fisher number, and grain-size particle-size distribution. It was found that there was significant variation from batch to batch. However, the pattern of the results suggested that this variability reflected the extent to which the particular sample had been handled up to the time of testing (the carbonyl powders are composed of relatively fragile filaments). In contrast, uniform characteristics were observed within a particular powder batch.

The sintering characteristics of these powders were determined in loose sintering experiments. The support screen normally present in battery plaques was omitted so that plaque characteristics could be measured more precisely. This phase of the work was also used to define test methods and to establish the interrelation of the physical characteristics of the plaque. The physical measurements made were thickness, porosity, shrinkage, resistivity, and mechanical strength. As expected of a sintering mechanism that consists of interparticle neck growth largely as a result of surface diffusion, the surface area, resistivity, and mechanical strength are linearly related. As a general test for uniformity, we recommend the measurement of mechanical strength by a four-point bend test. This test has the advantage that its sensitivity (unlike that of resistivity) is little affected by the presence of a support screen and it may be carried out more rapidly than the measurement of surface area.

Little difference in behavior was observed between the type 255 and 287 powders. Plaques of the same porosity obtained, for example, by sintering the 255 powder for a longer time than the 287 show comparable surface area, mechanical strength, and conductivity. In addition, in order to achieve highly uniform plaques, it would be advisable to use relatively long sintering times (e.g., 30 min). In the first few minutes of sintering, the physical characteristics change very rapidly with time. After approximately 20 min, the rate of change is minimal. The loss in porosity between 10- and 30-min sintering is approximately 5%; the increase in conductivity is a factor of three. More conductive plaques will minimize any intrinsic inhomogeneity under high drain rate operation.

Good reproducibility was obtained in the loose sintering process (thickness to ±0.0003 in., porosity to ±0.5%, surface area to ±3%) as long as the same regions of different plaques were compared. However, uniformity within a plaque was not good. Definite trends in physical properties across the plaques could be related to the leveling technique used in producing the plaques. Loose sintering was, therefore, not considered to be a practical method for producing uniform plaque.

During these studies, we also demonstrated that mercury porosimetry is fundamentally unsuitable as a means of defining pore-size distribution. The rapid increase in intruded volume at a particular pressure, often interpreted as a sharp pore-size distribution, is indicative only of a breakthrough pressure that is relatively insensitive to pore size.

For larger quantities of reproducible plaque, the slurry coating process is the preferred method of preparation: (1) the non free-flowing, carbonyl nickel powders are more easily handled in a slurry to give plaque of uniform thickness and porosity, and (2) slurry coating is a semicontinuous process rather than a batch process, such as loose sintering.

The principal practical problems encountered during the establishment of a slurry coating process for the preparation of nickel plaque were: (1) the removal of entrained air from the slurry, and (2) achieving homogeneity of the slurry mix. Plaques with good uniformity have been prepared, but reproducibility from preparation to preparation could not be guaranteed. Plaque for impregnation studies was selected from those preparations that gave uniform and reproducible values of thickness, porosity, and mechanical strength. During the following phases of the program, the slurry coating procedure was continuously improved.

The second phase of the program, discussed in detail in the previous annual report,[3] has considered the methods by which the active materials were incorporated into the nickel plaque to produce both positive and negative plates. The active material for the positive plate is precipitated as nickel hydroxide and for the negative plate as cadmium hydroxide. The purpose of the study of the various methods of impregnation was to determine which one offered the best control of the quantity and distribution of the active materials in the pore structure. Good distribution and also optimum morphology are important to effective utilization of the active material. Three basic processes were examined: (1) chemical conversion of the nitrates to the hydroxides, (2) the electrochemical conversion method first described by Fleischer, and (3) electrochemical impregnation at 25°C. The aim was to define the procedures and preparative conditions that would give rise to the most uniform components in a reproducible manner.

The variables considered were solution concentration for chemical conversion, current density for the Fleischer method, and the loading for both methods. These variables were chosen for more detailed study from a previous preliminary examination of impregnation methods. The plates were examined in terms of uniformity and reproducibility of weight gain, capacity, and utilization. The determination of utilization demanded chemical analysis of the active materials. Since analytical procedures are not well defined in the literature, significant effort was devoted to the development of reproducible and accurate analytical methods.

For negative plates, both the charged and discharged forms of the active material were readily determined since the ionic form [$Cd(OH)_2$] dissolves in ammoniacal NH_4Cl, whereas cadmium metal is unaffected. After separation, the two forms of cadmium were determined by EDTA titration.

A similar approach to the analysis of the positive electrode resulted in significant errors due to corrosion of the nickel substrate. A novel approach involving potentiostatic control of the plate during the extraction process successfully eliminated the corrosion problem, but its application was limited to analysis of the plate in the discharged state. For this reason and because both the charged and discharged species are soluble in any extraction solution, a separate determination of the state of charge was necessary. The method used depended on the determination of the active oxygen equivalent by reaction with potassium iodide and subsequent estimation of the iodine formed with sodium thiosulphate. It was established that it is critically important not to wash and dry the electrodes prior to analysis. Plaque corrosion is also another potential source of error in this determination. Specific techniques are described to minimize these errors. However, even with these precautions, determination of the state of charge by a chemical method still gave a figure lower than that defined by discharge. It is concluded, therefore, that the only guide to utilization of positive active material is a measurement of the amount of material that is not discharged (in terms of residual active oxygen) when the plate is in the nominally discharged state.

It was concluded from the experimental data collected on the impregnation methods that more uniform and reproducible plates were prepared by the chemical conversion process. For the positive plates, the less concentrated impregnation solution are to be preferred. No distinction could be drawn for the negatives. Plates prepared by the electrochemical process were noticeably lower in reproducibility and uniformity.

It should be stressed, however, that these were interim assessments, based on capacities measured after up to ten cycles, and have not included factors such as cycle life of behavior under sealed cell conditions.

It is also apparent from the data that uniformity and reproducibility of weight gain and capacity improve with loading, suggesting that there is a leveling effect (as might be expected). More surprisingly, utilization was found to be independent of loading up to quite high levels. From a limited amount of data, plaque thickness was found to have no influence on uniformity. Plaque corrosion during impregnation was more extensive for the chemical conversion process.

A more recent modification of the electrochemical impregnation method involving impregnation from nickel or cadmium nitrate solution at its boiling point, as described by McHenry[4] and Beauchamp,[5] was also made the subject of a study[6] which paralleled our previous examination of the chemical and electrochemical conversion process. The objective was, as before, to define the critical variables of the process and to optimize the conditions of impregnation in terms of uniformity and reproducibility at the highest possible specific capacity.

The most important finding regarding the high temperature electrochemical impregnation method was that the specific capacity attainable by this process was critically dependent on the physical characteristics of the porous nickel substrate. Under conditions of this investigation plaques prepared by a dry sintering technique had better characteristics for the high temperature electrochemical impregnation process than those prepared by slurry coating. The maximum stable capacity measured during cycling tests was 7.7 Ahr/in.^{3} for a positive plate and 7.4 Ahr/in.^{3} for a negative. Capacities in excess of 10 Ahr/in.^{3} were observed during the formation cycles of some of these plates. Complete experimental procedures are contained in a semiannual report.[6] It was also demonstrated that plaque corrosion was as little as 3% during the high temperature electrochemical impregnation process, compared to ~8% in both the conventional impregnation methods.

The third phase involved a comparative study of the different manufacturing methods. It is the subject of this report. This comparative study is set up as a factorially-designed experiment to examine the manufacturing variables, some of the operational variables, and any interaction that might exist between them. The manufacturing variables in the factorial design include plaque preparation method, plaque porosity and thickness, impregnation method, and loading. As operational variables, we investigated the effect of various charge and discharge rates.

II. EXPERIMENTAL DESIGN

A. Introduction

As will be apparent later, there is a large number of variables to examine in the experimental program. It is obvious that a sound statistical approach is essential in the program planning in order to extract the maximum useful information from the experimental results. The following represents a brief summary of the basic aspects of the factorial design of experiments and the analysis of the data so obtained.

It should be emphasized at the outset that we are seeking to define the influence of process and operating variables on plate performance and any interactions which occur between these two sets of variables. We are not simply looking for the extent of random changes that occur in a manufacturing or operating sequence. The latter aspect is easily accomplished by regression analysis and the definition of confidence limits. In the approach set out below, the intention is to make a quantitative assessment of the influence of the variables deliberately introduced in manufacture and operation. To achieve this, a full factorial experimental design is required.

B. Factorial Experimentation*

Factorial experiment is the name commonly applied to an experiment wherein we control several factors and investigate their effects at each of two or more levels. The experimental plan consists of taking an observation at each one of all possible combinations that can be formed for the different levels of the factors. Each such different combination is called a treatment combination.

Suppose that we are interested in investigating the effect of pressure and temperature on the yield of some chemical process. Pressure and temperature will be called the factors in the experiment. Each specific value of pressure to be included will be called a level of the pressure factor. In the past, one common experimental approach has been the so-called "one at a time" approach. This kind of experiment would study the effect of varying pressure at some constant

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* Freely adapted from NBS Handbook No. 91-Experimental Statistics by G. Natrella and Industrial Experimentation, H.M. Stationery Office, London.

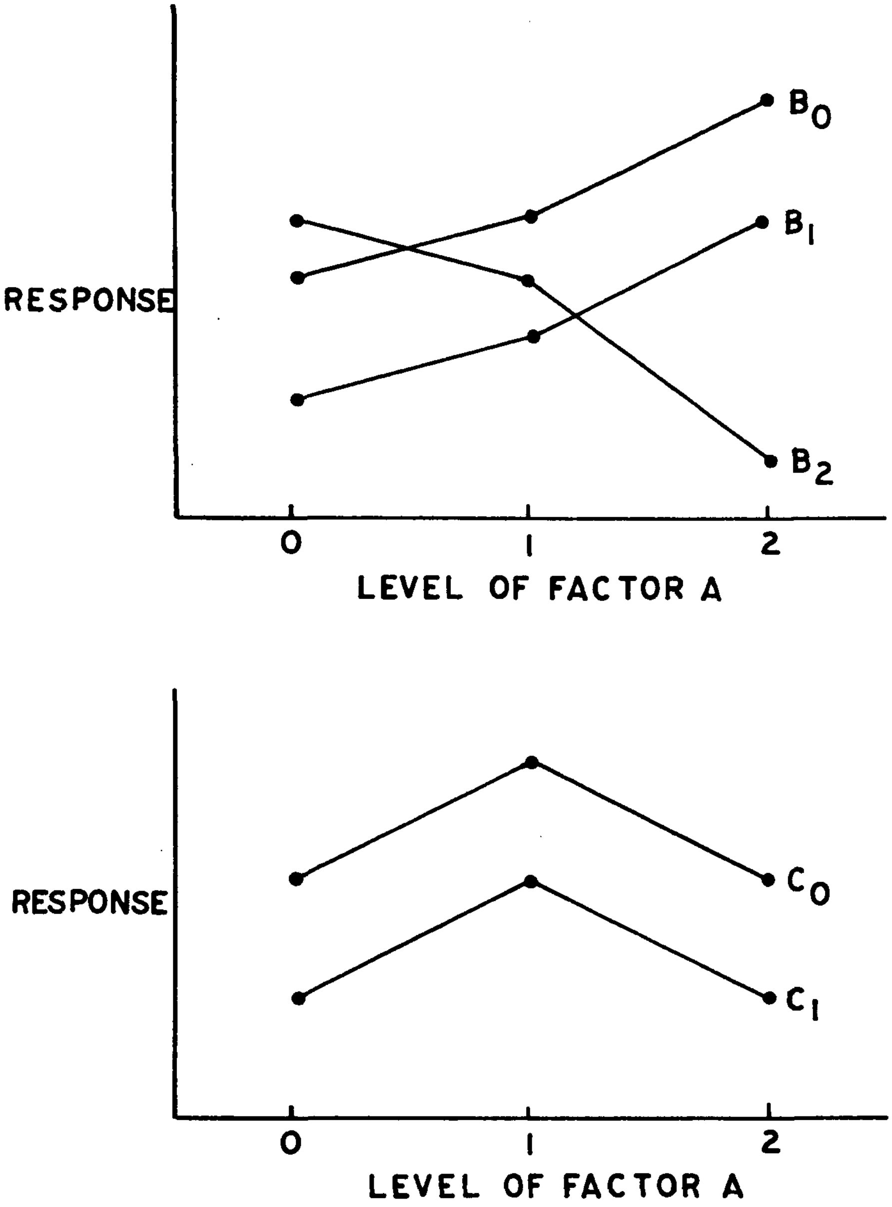
temperature and then study the effect of varying temperature at some constant pressure. Factors would be varied "one at a time." The results of such an experiment are fragmentary in the sense that we have learned about the effect of different pressures at one temperature only (and the effect of different temperatures at one pressure only). The reaction of the process to different pressures may depend on the temperature used; if we had chosen a different temperature, our observed relation of yield to pressure may have been quite different. In statistical language, there may be an interaction effect between the two factors within the range of interest, and the "one at a time" procedure does not enable us to detect it.

In a factorial experiment, the levels of each factor we wish to investigate are chosen, and a measurement is made for each possible combination of levels of the factors. Suppose that we had chosen two levels: say, 7 cm and 14 cm for pressure and 70°F and 100°F for temperature. There would be four possible combinations of pressure and temperature, and the factorial experiment would consist of four trials. In our example, the term level is used in connection with quantitative factors, but the same term is also used when the factors are qualitative.

In the analysis of factorial experiments, we speak of main effects and interaction effects (or simply interactions). Main effects of a given factor are always functions of the average response or yield at the various levels of the factor. In the case where a factor has two levels, the main effect is the difference between the responses at the two levels averaged over all levels of the other factors. In the case where the factor has more than two levels, there are several independent components of the main effect, the number of components being one less than the number of levels. If the difference in the response between two levels of factor A is the same regardless of the level of factor B (except for experimental error), we say that there is no interaction between A and B or that the AB interaction is zero. Fig. 1 shows two examples of response of yield curves; one example shows the presence of an interaction, and the other shows no interaction. If we have two levels of each of the factors A and B, then the AB interaction (neglecting experimental error) is the difference in the yields of A at the second level of B minus the difference in the yields of A at the first level of B. If we have more than two levels of either or of both A and B, then the AB interaction is composed of more than one component. If we have "a" levels of the factor A and "b" levels of the factor B, then the AB interaction has (a-1)(b-1) independent components.

For factorial experiments with three or more factors, interactions can be defined similarly. For instance, the ABC interaction is the interaction between the factor C and the AB interaction (or, equivalently, between the factor B and the AC interaction or A and the BC interaction).

As in any experiment, we must have a measure of experimental error to use in judging the significance of the observed differences in treatments. In the larger factorial designs, estimates of higher-order interactions will be available. The usual assumption is that high-order interactions are physically impossible and that the estimates so labelled are actually



Effect of different levels of A on the response for three different levels of B - interaction present

Effect of different levels of A on the response for two different levels of C - no interaction present

Fig. 1. Examples of response curves showing presence or absence of interaction

estimates of experimental error. As a working rule we often use third- and higher- order interactions for error. This does not imply that third-order interactions are always nonexistent. The judgement of the experimenter will determine which interactions may reasonably be assumed to be meaningful and which may be assumed to be nothing more than error. These latter interactions may be combined to provide an internal estimate of error for a factorial experiment of reasonable size. For very small factorials, e.g., 2^3 or smaller, there are no estimates of high-order interactions and the experiment must be replicated (repeated) in order to obtain an estimate of error from the experiment itself.

C. Procedures in Factorial Design

A factorial experiment in which we have n factors, each at two levels, is known as a 2^n factorial experiment. The experiment consists of 2^n trials, one at each combination of levels of the factors. To identify each of the trials, we adopt a conventional notation. A factor is identified by a capital letter and the two levels of a factor by the subscripts zero and one. If we have three factors, A, B, and C, then the corresponding levels of the factors are A_0, A_1; B_0, B_1; and C_0, C_1, respectively. By convention, the zero subscript refers to the lowest level, to the normal condition, or to the absence of a condition, as appropriate. A trial is represented by a combination of small letters denoting the levels of the factors in the trial. The presence of a small letter means that the factor is at the level denoted by the subscript one (the higher level for quantitative factors); the absence of a letter means that the factor is at the level denoted by the subscript zero (the lower level for quantitative factors). Thus, the symbol (a) represents the treatment combination where A is at the level A_1, B is at B_0, and C is at C_0. The symbol bc represents the treatment combination where A is at the level A_0, B is at B_1, and C is at C_1. Conventionally, the symbol (1) represents the treatment combination with each factor at its zero level. In an experiment with three factors, each at two levels, the $2^3 = 8$ combinations, and thus the eight trials are represented by (1), a, b, ab, c, ac, bc, abc. For four factors, the trials are as shown in Table I.

Table I. Factorial Terms for Four Factor Experiment

		A_0		A_1	
		B_0	B_1	B_0	B_1
C_0	D_0	(1)	b	a	ab
	D_1	d	bd	ad	abd
C_1	D_0	c	bc	ac	abc
	D_1	cd	bcd	acd	abcd

Yates' method is a systematic method for obtaining estimates of main effects and interactions for two-level factorials. The method was originally described by Yates[7] and may be found in various textbooks (Cochran and Cox[8] and Davies[9]). In the Yates' procedure the treatment combinations are listed in standardized order, and after following the prescribed procedure, estimated main effects and interactions result. The order in which the treatment combinations are listed determines the order of estimated effects.

The standard order for four factors is (Table I): (1), a, b, ab, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, abcd.

The estimated main effects and interactions for four factors also appear in a standard order:

T, A, B, AB, C, AC, BC, ABC, D, AD, BD, ABD, CD, ACD, BCD, ABCD, etc.,
where T corresponds to the overall average effect, A to the main effect of factor A, AB to the interaction of factors A and B, etc.

In Appendix A, the detailed steps involved in Yates' procedure for obtaining estimates of main effects and interactions for two-level factorials are given. They are further illustrated in an example analysis of a four-factor experiment as shown in Table I. Procedures for testing the significance of main effects and interactions are also included.

D. Experimental Program

1. Manufacturing variables

The comparative study of the manufacturing variables was set up as a four-factor experiment, with two factors at three and two factors at two levels.

The variables were:

A (plaque type) at three levels
  A_0 - Loose powder sinter with screen substrate
  A_1 - Slurry-coated screen
  A_2 - Slurry-coated perforated sheet

B (plaque thickness) at two levels
  B_0 - 20 mil
  B_1 - 30 mil

C (impregnation method) at three levels
  C_0 - Chemical conversion
  C_1 - Electrochemical conversion
  C_2 - High temperature electrochemical impregnation

D (loading level) at two levels
  D_0 - 5 Ahr/in.^{3}
  D_1 - 8 Ahr/in.^{3}

The factorial design was then set out as in Table II. This approach involved 36 experiments which were carried out in duplicate for both positive and negative plates.

Table II. Factorial Design for Manufacturing Variables

		A_0		A_1		A_2	
		B_0	B_1	B_0	B_1	B_0	B_1
C_0	D_0	(1)	b	a_1	a_1b	a_2	a_2b
	D_1	d	bd	a_1d	a_1bd	a_2d	a_2bd
C_1	D_0	c_1	bc_1	a_1c_1	a_1bc_1	a_2c_1	a_2bc_1
	D_1	c_1d	bc_1d	a_1c_1d	a_1bc_1d	a_2c_1d	a_2bc_1d
C_2	D_0	c_2	bc_2	a_1c_2	a_1bc_2	a_2c_2	a_2bc_2
	D_1	c_2d	bc_2d	a_1cd	a_1bc_2d	a_2c_2d	a_2bc_2d

A_0 - dry sinter plaque (D)
A_1 - slurry-coated plaque, Ni screen substrate (S)
A_2 - slurry-coated plaque, perforated sheet substrate (P)
B_0 - thin plaque
B_1 - thick plaque
C_0 - chemical conversion method
C_1 - electrochemical conversion method
C_2 - high temperature electrochemical impregnation
D_0 - low loading with active material
D_1 - high loading with active material

The basis for comparison was the behavior during a low earth orbit dury cycle 30/60 min cycle) with 25% depth of discharge.

2. Operational variables

A comparative study was carried out to examine the effect of various charge and discharge rates on differently prepared electrodes. The experiments were set up as two factor factorials, with each factor at three levels as shown in Table III.

The factors were:

A (charge rate) at three levels

A_0 - C/20 rate
A_1 - C/6 rate
A_2 - C/2 rate

B (discharge rate) at three levels

B_0 - C/5 rate
B_1 - C rate
B_2 - 5C rate

Five different preparations were examined in duplicate for both positive and negative plates.

Table III. Factorial Design for Operational Variables

	A_0	A_1	A_2
B_0	1	a_1	a_2
B_1	b	a_1b	a_2b
B_2	b_2	a_1b_2	a_2b_2

III. PLAQUE PREPARATION

A. Slurry Coating Process

1. Introduction

The most common process for preparing nickel plaque for battery plates is based on coating a screen or perforated strip with a suspension of carbonyl nickel powder in a viscous medium. This process has two major advantages over loose sintering: (1) the handling of the powder as an aqueous suspension overcomes the difficulties associated with its non free-flowing characteristics, a factor that leads to nonuniformity in loose sintering, and (2) it is a continuous process that provides better control over plaque properties and improved reproducibility.

The viscous medium used to suspend the nickel powder is usually a solution of methyl cellulose or carboxymethyl cellulose. This binds the powder on drying and then burns off in the sintering process to leave a negligible residue.

2. Slurry preparation

The slurry coating process is not without technical difficulties. The principal problems are: (1) to avoid entrainment of air, and (2) to obtain a slurry of homogeneous and reproducible properties.

The first problem is a result of the low bulk density of the powder and the relatively high viscosity (~1300 cps) of the 3% methyl cellulose solutions. The second is twofold. Vigorous mixing to attain homogeneity can introduce air into the mixture and can change the physical characteristics of the relatively fragile filamentary nickel powder.

The following approach has resulted in the preparation of satisfactory slurries in the laboratory. The required quantities of nickel powder (sieved through 54 mesh to remove large agglomerates) and dry methyl cellulose were dry mixed. (Typically, we used 1075 g of INCO-type 287 carbonyl nickel powder and 27.5 g of Methocel 90HG-400, Dow Chemical Co.) The mixing was carried out in a large cylindrical container rotated on a roll mixer at about 20 rpm for 1 to 4 hr. The powder mixture was cascaded into the required amount of hot (85 to 90°C) deionized water under manual stirring. Hot water ensured complete wetting of the powders, since the methyl cellulose is insoluble at the higher temperature. The mixture was manually stirred at approximately 5-min intervals until it thickened to a firm consistency with no bleeding out of the water. At this point the appearance was very granular, with the individual Methocel particles swollen but well distributed. This mixture was then cooled to 5°C under occasional stirring. On cooling, the methyl cellulose dissolved to give a highly viscous slurry. It was kept below 10°C for 20 to 30 min and continuously mixed. To prevent evaporation losses the container was then loosely sealed and transferred to a vibratory shaker (New Brunswick Scientific, Model G33 Gyrotary Shaker) for a period of 12 to 16 hr. During this step remaining traces of air were slowly released. It further prevented the slurry from settling. A sufficient yet gentle stirring effect was obtained with 2 ℓ beakers. Therefore, larger quantities of slurry were prepared in separate batches of the above-mentioned size. Typical values for the viscosity of the final slurry were between 150,000 and 180,000 cps.

3. Coating process

The slurry was applied to the screen by passing it under the roller of a slurry box mounted in a pulling rig. The design of the slurry box is shown in Fig. 2. The screen left the slurry box vertically and passed between doctor blades which determine the thickness of the coating. The coating was allowed to air dry. Generally 6 to 7 ft of usable plaque were obtained in a run. The pulling speed was adjustable from 1 to 30 in./min. Most plaques were prepared at a speed of 1 to 1.5 in./min. Only the thicker coatings on perforated sheet substrate were carried out at 6 in./min to obtain a higher shear rate and thus an increased viscosity.

The principal problem associated with the plaque preparation was the achievement of a uniform and predictable coating thickness, particularly since the screen or perforated sheet should be coated uniformly on both sides. As will be shown later, a centered substrate does not effect the measurement of mechanical strength by a four-point bend test. A main problem we were faced with was the poor quality of the substrate material, which contained bends, bows, and kinks, making centering between the doctor blades very difficult despite the employment of shim guides at the outside edges of the screen. In order to remove, as best possible, bends and bows, each 11-ft piece was rolled with a 2-in. diameter cylinder prior to use.

During the coating process the room temperature was controlled between 70 and 75°F and the relative humidity was kept below 60%. Earlier experiments had shown that elevated temperature (85 to 95°F) and humidity (above 60% RH) could cause thinning and running of the coating during application.

Typically, a doctor blade setting of 0.055 in. produced a green plaque of 0.040 in. after drying and a sintered plaque of 0.030 in. The green plaque was cut into sections of 13 in. length and sintered in a BTU furnace in an atmosphere of pure dry hydrogen (30 min at 900°C).

B. Loose Powder Sintering

Ni powder layups were prepared on polished quartz plates as follows: shims having half the thickness of the desired layup were placed on two opposite edges of a polished quartz plate (6 × 4 in.) The powder was sieved onto the plate through a 54 mesh screen and leveled with a doctor blade. Then the screen was placed onto the powder layup, the shims were replaced by those equal to the final thickness, and the sieving and leveling procedure was prepared.

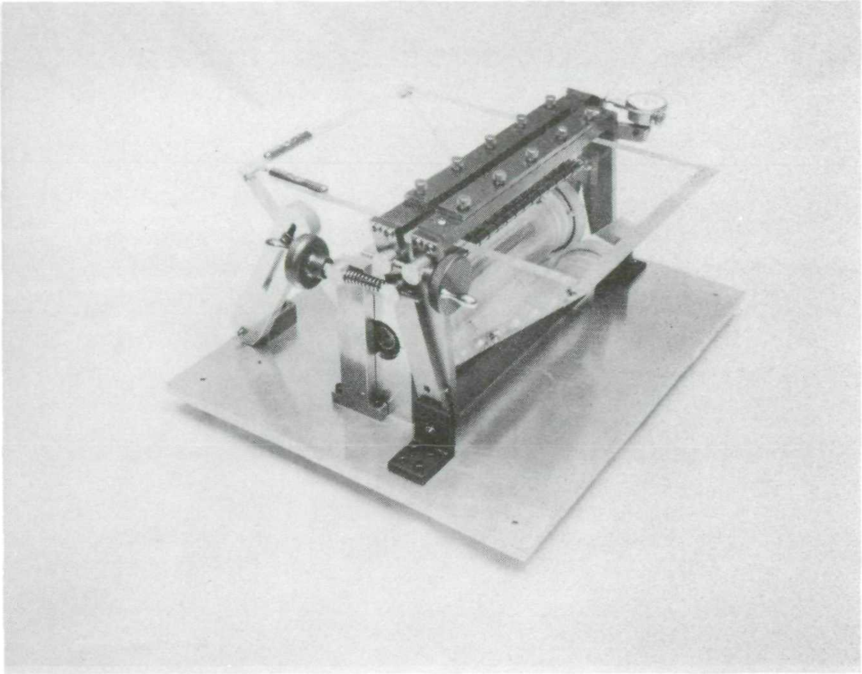


Fig. 2. Slurry-coating box

The most difficult task in this plaque preparation was the leveling of the powder with a steel straight edge. Because of the poor flow characteristics of the filamentary carbonyl powder, the buildup in front of the blade can cause compaction, tearing (cracking), or under-cutting of the surface unless extreme care is taken. The technique that was used consisted of holding the striking blade parallel to the 4-in. edge of the mold and moving it in a zig-zag pattern across the mold. This approach has the advantage that the excess powder is removed at the sides of the plaque and does not build up excessively in front of the striking blade.

The loose powder layups were sintered in a BTU furnace at 900°C in an atmosphere of pure dry hydrogen. The sintering was carried out in two periods of 20 min each. After the first sintering, the plaque was quickly lifted from the quartz plate. By this procedure, sticking of the nickel plaque to the quartz plate, which was observed after a longer one-step sintering could be avoided.

IV. PLAQUE CHARACTERIZATION

A. Introduction

A detailed investigation of various methods used to characterize nickel plaques was carried out earlier.[2] It included the measurement of area and volume shrinkage, porosity and pore-size distribution, surface area, resistivity, and mechanical strength. Here we limited the characterization of the Ni plaques to the measurement of thickness, porosity, electrical resistivity, and mechanical strength. The thickness and porosity were determined directly on the plaque used for further impregnation and testing. The electrical conductivity and mechanical strength were measured on a sample (1 in. × 2 in.) obtained from a section adjacent to the plaque to be used further.

B. Thickness and Porosity

The thickness was determined at 5 positions of the plaque (2 in. × 2 in.) using a micrometer. The apparent plaque porosity was obtained from the measured dimensions and the plaque weight. The sinter porosity was calculated from this value by taking into consideration the weight and volume of the substrate (screen or perforated sheet). A certain inaccuracy in the absolute values of the porosities was introduced by the fact that the plaque surface was not perfectly flat since the pattern of the support screen was apparent to some extent.

C. Electrical Resistivity

Resistivity was measured by a four-electrode method. Current-carrying electrodes were attached to the full length of opposite edges of a plaque approximately 5 cm by 2 cm. The resistivity was determined by measuring the potential difference between two points a known distance apart on a line perpendicular to the edges in contact with the current-carrying electrodes. The resistivity was then calculated knowing the current and the cross-sectional area of the plaque. This method of measurement avoids contributions from contact resistance, and it was possible to check that the current distribution was uniform in the region of the plaque where the measurements were made.

D. Mechanical Strength

Like the electrical resistivity, a mechanical test is an indicator for the development of particle-to-particle bonds in the sintered structure. Unlike the measurement of electrical resistivity, a mechanical test in the bending mode, as opposed to a straight tensile test, can be carried out to virtually eliminate the effects of a support in the center of the plaque. In bending, a 20-mil plaque containing a 10-mil screen in its center will reflect the strength of the sintered nickel outer layers, since 90% of the load is supported by stresses in these layers.

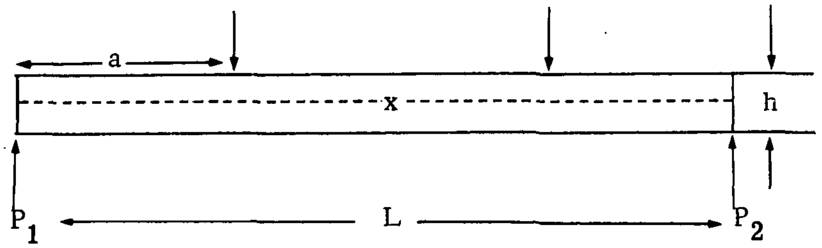
Fig. 3 is a photograph of the completed bending jig. The gauge length between the lower supports is 1 in., with the load applied at the quarter points. Four-point bending experiments are preferred to three-point tests, since the conditions at the center of the specimen length more nearly approach pure bending. The load is applied with the circular pins shown in the figure which are 1/8 in. in diameter.

This bending jig is used in a constant crosshead motion testing machine (Instron). The test is carried out by placing a sample, thin compared to its length, across the outer supports of the lower fixture. The fixture supporting the upper loading points is rigidly attached to the crosshead of the machine, while the lower fixture supporting the sample is placed on a flat topped compression load cell (Instron model CC load cell, 0 to 60 psi).

During the test, the crosshead is driven downward, bending the sample. The displacement causes a load which is recorded as a function of time. Since the rate of deflection is known, this also gives the load as a function of the deflection. This trace (Fig. 4) shows that initially there is a linear increase of load, followed by a region of decreasing rate, and finally an abrupt dropoff of the load corresponding to the failure strength of the material. This also corresponds to cracking. The point at which the curve becomes concave downward marks the onset of plastic yielding. The load at this time is typically 3 to 4 lbs.

The stresses and strains at any point on the linear part of this trace may be determined exactly. In the plastic portion, above the yield stress, the stress may only be calculated approximately.

If the bending moments are examined,



with:

$$P_1 = P_2 = \frac{P_{total}}{2};$$

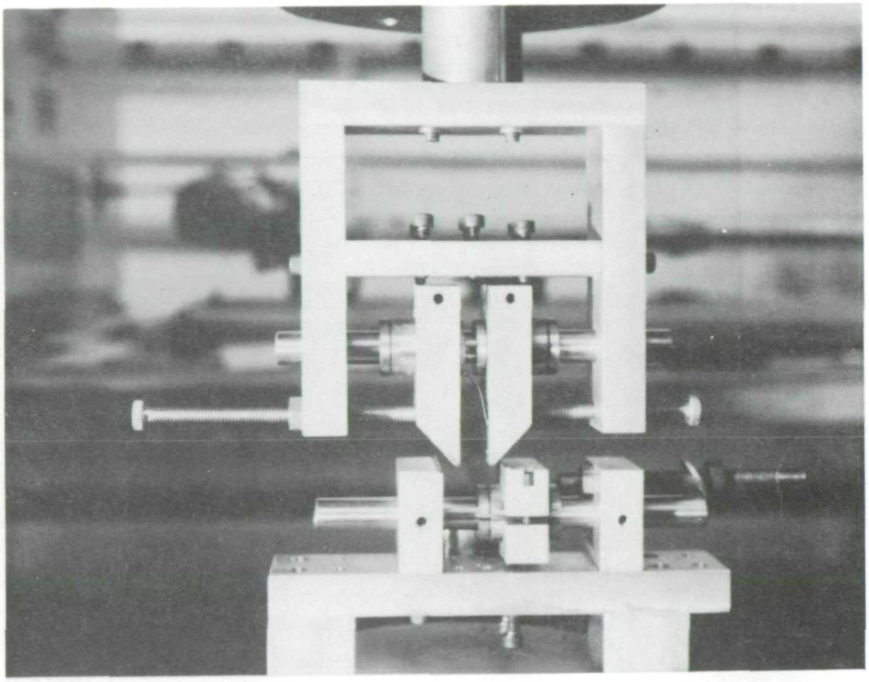


Fig. 3. Four-point bend test apparatus

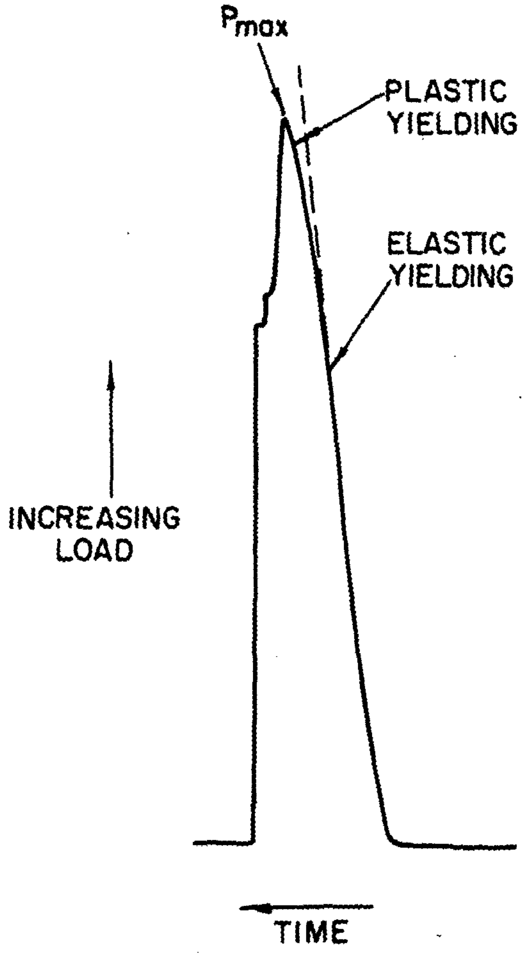


Fig. 4. Bend test LN 13

then, the bending moment, M_b, equals $\frac{P}{2} \times a$ or $\frac{P \times L}{8}$, since $a = \frac{L}{4}$. The stress, δ, is given by:

$$\delta = \frac{M_b \times y}{I_{yy}}$$

where y is half the thickness and h is half the sample; i.e., it defined the point of zero moment, x. I_{yy}, the moment of inertia, equals $\frac{bh^3}{12}$ for a plaque of width b. Thus:

$$\delta = \frac{3}{4} \times \frac{PL}{bh^2} \qquad (1)$$

where δ = stress (psi)
P = load (lbs)
L = distance between outer supports
b = width of sample
h = thickness of sample.

Note that this applies only when the inner pins are at the quarter points and $h << a$.*

This is the maximum stress in the outermost layers of the sample. The stress so calculated is called the modulus of rupture os simply the maximum tensile stress at failure.

The strain corresponding to any stress is obtained from Hooke's law:

$$\epsilon = \frac{3}{4} \frac{PL}{E'bh^2} \qquad (2)$$

where E' is the effective modulus of the porous nickel. This is related to the Young's modulus for pure nickel ($E = 30 \times 10^{-6}$ lb/in.^{2}) by:

$$E' = (1 - \text{fraction porosity})\ E. \qquad (3)$$

E. Results

The plaque data for the various electrodes tested are included in Table IV. As expected from a sintering process that involves neck growth between the individual particles the sinter porosity, the mechanical strength and the electrical resistivity correlate well.

Average values for the sinter porosity, the mechanical strength, and the sinter resistivity for the various plaque types and thicknesses are summarized in Table V. Aside from the

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*For other symmetries, e.g., inner pins are at a distance, ℓ, apart:

$$\delta = \frac{3\ Pa}{bh^2}$$

where a is now $1/2\ (L - \ell)$.

value for the thin slurry-coated plaque on screen, the average porosities were independent of plaque thickness and little difference was observed between slurry-coated plaque containing perforated sheet or nickel screen as substrate. The high calculated value for the thin slurry-coated plaque does not reflect a true sinter porosity. It is the consequence of the uneven plaque surface caused by the structure of the screen substrate which leads to an error in the measurement of true plaque thickness. The surfaces of the other plaques were fairly flat and caused no comparable problems. The loose sintered plaque showed a considerably higher average sinter porosity of 81.4% compared to the 79.3% of slurry-coated plaques. The corresponding differences appear also in the values for the mechanical strength and the sinter resistivities. The average values obtained for the mechanical strength were 67.5 kg/cm^2 and 94 kg/cm^2 for loose-sintered and slurry-coated plaque, respectively. The centered substrate material is of no consequence, which confirms that the mechanical strength measured by a four-point bend test is a suitable parameter for plaque characterization and truly reflects the strength of the sintered powder structure. The electrical resistivity of the sintered powder correlates also with the sinter porosity. The measured average values were $2.1 \times 10^{-4} \Omega \cdot cm$ for loose-sintered and $1.5 \times 10^{-4} \Omega \cdot cm$ for slurry-coated plaque. The measurement of conductivity is, however, a less suitable parameter for characterization of the porous sinter structure since a significant part of the current passes through the substrate and its mathematical consideration increases the error margin in the sinter resistivity of the plaque.

Within the narrow margin of sinter porosity variations, a correlation between it and mechanical strength as well as electrical powder resistivity has been determined from the measured data by a least squares analysis. The results are graphically shown in Fig. 5.

Table IV. Plaque Properties

CHEMICAL CONVERSION

Treatment Combination	Plate*	Thickness (mils)	Porosity		Mech Strength Kg/cm^2	Resistivity	
			Apparent Porosity (%)	Sinter Porosity (%)		Apparent $\Omega \cdot cm \times 10^{-4}$	Sinter $\Omega \cdot cm \times 10^{-4}$
1	619-4-11A 619-4-13A 20-D-5	22.4 22.2	74.9 75.3	81.7 80.7	69.2 83.7	.94 1.94	2.0 5.0
b	619-4-1A 619-4-23A 30-D-5	31.7 30.6	76.2 76.7	80.1 81.3	84.5 44.8	1.48 1.3	2.2 2.2
a_1	20-S-5						
a_1b	598-26-1C A 598-25-1A A 30-S-5	25.0 27.9	75.5 71.1	80.0 75.9	97.5 106.2	1.13 1.12	1.6 1.3
a_2	598-36-1A A 598-36-1A B 20-P-5	23.1 24.3	74.6 74.6	79.2 79.2	82 82	.72 .75	1.6 1.6
a_2b	598-29-1B A 598-29-1B B 30-P-5	30.1 30.0	73.4 77.0	82.6 79.0			
d	619-4-11B 619-4-13B 20-D-8	21.9 22.2	74.9 75.3	81.7 80.7	69.2 83.7	.92 1.94	2.0 5.0
bd	619-4-1B 619-4-23B 30-D-8	31.6 30.7	76.2 76.7	80.1 81.3	84.5 44.8	1.48 1.30	2.2 2.2
a_1d	20-S-8						
a_1bd	598-26-1C B 598-25-1A B 30-S-8	25.6 28.0	75.5 71.1	80.0 75.9	97.5 106.2	1.13 1.12	1.6 1.3
a_2d	20-P-8						
a_2bd	598-29-1A A 30-P-8	31.6	73.4	82.6	108	.78	1.4

ELECTROCHEMICAL CONVERSION

Treatment Combination	Plate*	Thickness (mils)	Porosity		Mech Strength Kg/cm^2	Resistivity	
			Apparent Porosity (%)	Sinter Porosity (%)		Apparent $\Omega \cdot cm \times 10^{-4}$	Sinter $\Omega \cdot cm \times 10^{-4}$
c_1	619-4-39A 619-4-42B 20-D-5	21.8 22.0	75.8 74.9	80.9 81.7	80.3	1.21	1.9
bc_1	619-4-43A 619-4-44A 30-D-5	31.2 29.2	77.5	81.5	72.1	1.32	2.0
a_1c_1	598-35-1C A 598-35-1B A 20-S-5	24.9 24.3	78.1 76.8	83.1 82.3	94.5 90.6	1.18 1.14	1.8 1.6
a_1bc_1	598-34-1B A 598-33-4C A 30-S-5	26.9 26.4	73.3 75.5	78.0 80.2	117.0 98	.70 1.02	1.0 1.4
a_2c_1	20-P-5						
a_2bc_1	598-34-1D B 598-29-1D B 30-P-5	32.8 29.2	74.2 72.5	78.6 77.6	99.4 134.5	.77 .73	1.7 1.3
c_1d	619-4-39B 619-4-42A 20-D-8	21.5 21.9	75.8 74.9	80.9 81.7	80.3	1.21	1.9
bc_1d	619-4-43B 619-4-44B 30-D-8	31.2 28.9	76.2 77.5	80.1 81.5	72.1	1.32	2.0
a_1c_1d	598-35-1C B 598-35-1B B 20-S-8	24.6 24.9	78.1 76.8	83.1 82.3	94.5 90.6	1.18 1.14	1.8 1.6
a_1bc_1d	598-34-1B B 598-33-4C B 30-S-8	26.5 27.9	73.3 75.5	78.0 80.2	117 98	.78 1.02	1.0 1.4
a_2c_1d	20-P-8						
a_2bc_1d	598-34-1D A 598-29-1D A 30-P-8	33.8 29.8	74.2 72.5	78.6 77.6	99.4 134.5	1.13 .73	1.8 1.3

Table IV. (Continued)

HIGH TEMPERATURE ELECTROCHEMICAL IMPREGNATION

Treatment Combination	Plate*	Thickness (mils)	Porosity		Mech Strength Kg/cm^2	Resistivity	
			Apparent Porosity (%)	Sinter Porosity (%)		Apparent Ω . cm ×10^{-4}	Sinter Ω cm ×10^{-4}
c_2	619-4-23A 619-4-24A 20-D-5	22.3 22.1	76.7 78.6	81.3 81.5	44.8 71.7	1.79 1.23	3.2 2.0
bc_2	619-4-29A 619-4-31A 30-D-5	35.1 36.7	76.8 80.7	83.3 84.4	64.4 42.5	1.41 1.83	1.9 2.7
a_1c_2	598-32-1C A 598-32-1B A 20-S-5	24.3 24.6	78.1 78.1	83.8 83.8			
a_1bc_2	598-34-1A A 598-34-1D A 30-S-5	26.9 26.8	72.9 74.2	77.5 78.6	96.8 99.4	1.09 1.13	1.3 1.6
a_2c_2	598-26-1C A 598-27-1C A 20-P-5	25.6 23.0	75.5 71.6	80.0 79.1	97.5 95	.75 .72	1.3 1.6
a_2bc_2	598-33-3C A 598-33-3D A 30-P-5	27.3 27.8	75.0 74.4	79.5 79.2	94 93.1	.78 .70	1.4 1.3
c_2d	619-4-23B 619-4-24B 20-D-8	21.5 21.5	76.7 78.6	81.3 81.5	44.8 71.7	1.79 1.23	3.2 2.0
bc_2d	619-4-29B 619-4-31B 30-D-8	35.9 36.7	76.8 80.7	83.3 84.4	64.4 42.5	1.44 1.83	1.9 2.7
a_1c_2d	598-32-1C B 598-32-1B B 20-S-8	24.7 25.1	78.1 78.1	83.8 83.3			
a_1bdc_2	598-34-1A B 598-34-1D B 30-S-8	26.9 26.5	72.9 74.2	77.5 78.6	96.8 99.4	1.09 1.13	1.3 1.6
a_2c_2d	598-26-1C B 598-27-1C B 20-P-8	26.1 23.4	75.5 71.6	80.0 79.1	97.5 95	.75 .72	1.3 1.6
a_2bc_2d	598-33-3C B 598-33-3D B 30-P-8	27.3 28.5	75.0 74.4	79.5 79.2	94 93.1	.78 .70	1.4 1.3

CHEMICAL CONVERSION

Treatment Combination	Plate*	Thickness (mils)	Porosity		Mech Strength Kg/cm^2	Resistivity	
			Apparent Porosity (%)	Sinter Porosity (%)		Apparent Ω . cm ×10^{-4}	Sinter Ω • cm ×10^{-4}
1	619-4-18A 619-4-22A 20-D-5	23.5 21.8	76.7 76.5	81.6 82.3	57.5 56.4	1.2 1.21	1.9 2.0
b	619-4-26A 619-4-28A 30-D-5	30.6 38.6	76.5 78.6	80.6 82.1	75.5 57.5	1.11 1.45	1.5 3.7
a_1	20-S-5						
a_1b	598-26-2A A 598-25-1C A 30-S-5	26.7 28.1	76.5 76.9	80.9 81.2	84.4 65.5	1.36 1.06	2.0 1.5
a_2	598-28-1C A 598-28-1C B 20-P-5	21.4 24.3	71.8 71.8	78.2 78.2	107.5 107.5	.65 .74	1.4 1.6
a_2b	598-29-1C A 598-29-1C B 30-P-5	29.6 30.2	77.0 77.0	79.0 79.0	110.5 110.5	.74 .74	1.3 1.3
d	619-4-18B 619-4-22B 20-D-8	23.8 21.7	76.7 76.5	81.6 82.3	57.5 56.4	1.2 1.21	1.9 2.0
bd	619-4-26B 619-4-28B 30-D-8	31.2 39.0	76.5 78.6	80.6 82.1	75.5 57.5	1.13 1.45	1.5 3.7
a_1d	20-S-8						
a_1bd	598-26-2A B 598-25-1C B 30-S-8	26.9 28.2	76.5 76.9	80.9 81.2	84.4 65.5	1.36 1.06	2.0 1.5
a_2d	20-P-8						
a_2bd	598-29-1A B 30-P-8	28.5	73.4	79.0	108.0	.70	1.2

Table IV. (Continued)

	Treatment Combination	Plate	Thickness (mils)	Porosity		Mech Strength Kg/cm^2	Resistivity	
				Apparent Porosity (%)	Sinter Porosity (%)		Apparent Ω . cm × 10^{-4}	Sinter Ω . cm × 10^{-4}
ELECTROCHEMICAL CONVERSION	c_1	619-4-40A 619-4-45A 20-D-5	21.5 21.2	75.9 76.1	81.6 81.8	76.2 75.4	1.11 1.14	1.6 1.8
	bc_1	619-4-46A 619-4-47A 30-D-5	30.3 31.4	76.8 76.7	80.8 81.3	83.6	1.23	1.8
	a_1c_1	598-35-1A A 598-35-2A A 20-S-5	25.0 25.5	77.4 74.1	82.4 80.3	92.9 81.6	1.17 1.24	1.6 2.0
	a_1bc_1	598-33-4B A 598-33-4D A 30-S-5	27.3 28.1	74.7 75.2	79.1 79.9	103.0 104.5	.94 1.09	1.2 1.3
	a_2c_1	20-P-5						
	a_2bc_1	598-34-1A A 30-P-5	32.8	72.9	77.5	96.8	.66	1.4
	dc_1	619-4-40B 619-4-45B 20-D-8	22.5 21.8	75.9 76.1	81.6 81.8	76.2 75.4	1.11 1.14	1.6 1.8
	bdc_1	619-4-46B 619-4-47B 30-D-8	29.6 31.4	76.8 76.7	80.8 81.3	83.6	1.23	1.8
	a_1dc_1	598-35-1A B 598-35-2A B 20-S-8	24.2 25.3	77.4 74.1	82.4 80.3	92.9 81.6	1.17 1.24	1.6 2.0
	a_1bdc_1	598-33-4B B 30-S-8	26.8	74.7	79.1	103.0	.94	1.2
	a_2dc_1	20-P-8						
	a_2bdc_1	598-34-1A B 30-P-8	31.5	72.9	77.5	96.8	.66	1.4

	Treatment Combination	Plate	Thickness (mils)	Porosity		Mech Strength Kg/cm^2	Resistivity	
				Apparent Porosity (%)	Sinter Porosity (%)		Apparent Ω . cm × 10^{-4}	Sinter Ω . cm × 10^{-4}
HIGH TEMPERATURE ELECTROCHEMICAL IMPREGNATION	c_2	619-4-21A 619-4-37A 20-D-5	21.5 24.5	74.5 76.3	79.9 81.4	94.3 54.8	1.56 1.46	3.3 2.5
	bc_2	619-4-33A 619-4-34A 30-D-5	32.1 31.0	75.5 76.7	80.1 81.3	66.4	1.33	1.8
	a_1c_2	598-32-1A A 619-4-48A 20-S-5	24.9 24.6	78.1 76.8	82.8 82.3	95.8	1.18	1.6
	a_1bc_2	598-33-4A A 598-34-1C A 30-S-5	28.0 26.8	74.3 73.6	79.0 78.0	100.5 90.0	1.09 1.25	1.4 1.8
	a_2c_2	598-27-1A A 598-27-2C A 20-P-5	22.1 23.1	72.5 74.4	79.7 81.4	94.0 62.5	.69 .75	1.5 1.9
	a_2bc_2	598-33-3A A 598-33-3B A 30-P-5	28.8 29.0	76.9 75.9	80.9 80.1	91.8 96.1	.75 .85	1.4 1.6
	dc_2	619-4-21B 619-4-37B 20-D-8	21.9 25.0	74.5 76.3	79.9 81.4	94.3 54.8	1.56 1.46	3.3 2.5
	bdc_2	619-4-33B 619-4-34B 30-D-8	31.7 30.9	76.4	80.4	64.4	1.27	1.7
	a_1dc_2	598-32-1A B 619-4-48B 20-S-8	25.3 23.7	78.1 76.8	82.8 82.3	95.8	1.18	1.6
	a_1bdc_2	598-33-4A B 598-34-1C B 30-S-8	27.2 26.7	74.3 73.6	79.0 78.0	100.5 90	1.09 1.25	1.4 1.8
	a_2dc_2	598-27-1A B 598-27-2C B 20-P-8	21.9 22.8	72.5 74.4	79.7 81.4	94 62.5	.69 .75	1.5 1.9
	a_2bdc_2	598-33-3A B 598-33-3B B 30-P-8	28.3 28.6	76.9 75.9	80.9 80.1	91.8 96.1	.74 .85	1.4 1.6

*First two lines = identification numbers

Third line = identification code: Nominal thickness (mils) – plaque type – Nominal plate loading (Ahr/in.^{3}); D = loose sinter plaque, screen substrate, S = slurry-coated plaque, screen substrate; P = slurry-coated plaque, perforated sheet substrate

Table V. Average Values for Plaque Porosity, Mechanical Strength, and Resistivity

Plaque		Sinter Porosity (%)	Mechanical Strength (kg/cm^2)	Sinter Resisvitiy $\Omega \cdot$ cm $\times 10^{-4}$	Number of Measurements		
					SP	MS	SR
Loose sinter	thin	81.4	69.5	2.4	24	11	11
	thick	81.5	65.6	1.9	22	9	9
Slurry on screen	thin	82.6	91.1	1.7	16	5	5
	thick	79.0	96.6	1.5	23	12	12
Slurry on perforated sheet	thin	79.6	89.8	1.6	12	6	6
	thick	79.4	102.7	1.4	20	9	9

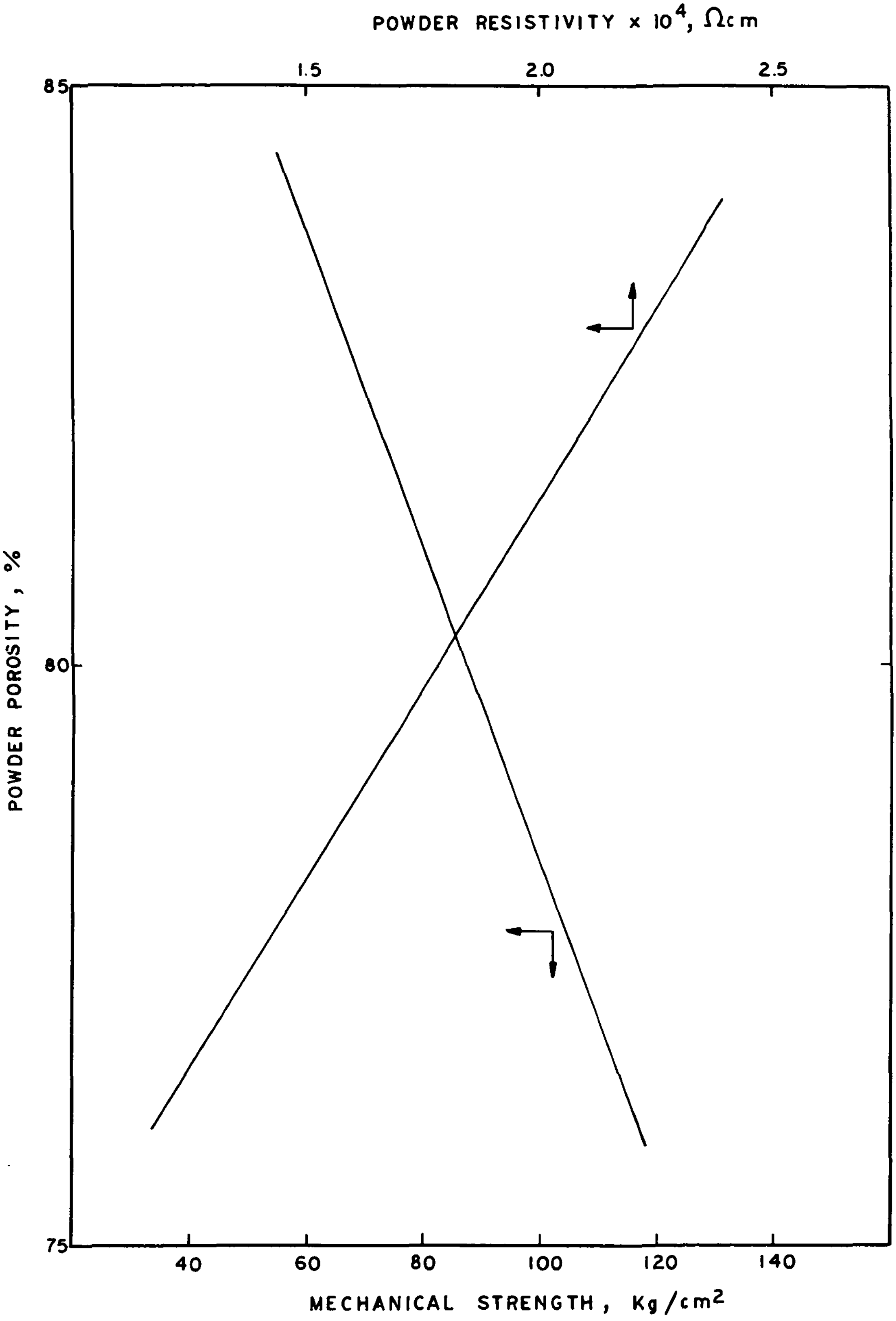

Fig. 5 Correlation of mechanical strength and powder resistivity with powder porosity of the sintered nickel plaque

V. PLAQUE IMPREGNATION

A. Introduction

The active material for positive plates is precipitated as nickel hydroxide and for the negative plates as cadmium hydroxide. Several procedures can be used to incorporate the active material into the nickel plaque. The most commonly used procedure is the chemical conversion method which involves the impregnation of the nickel plaque with the nitrate salt followed by conversion to the hydroxide. In commercial use is also a variation of this process which involves the passage of a cathodic current through the plaque during conversion of the nitrate to the hydroxide. It is designated here as electrochemical conversion. The high temperature electrochemical impregnation is a recently developed procedure in which the hydroxide is electrochemically precipitated in the plaque structure in a one-step process.

All impregnations were carried out with 2- × 2-in. plaques. Tabs were in the form of two 1/4-in. wide, 0.004-in. thick nickel strips spot welded on either side of one edge of the plaque where the porous nickel had been removed to expose the support screen. A further length of the same nickel strip up to 6 in. long was then spot welded to the center point of the previous nickel strips and perpendicular to them. This arrangement of the tab was intended to ensure as uniform a current density as possible during the impregnation and testing.

B. Chemical Conversion Method

The equipment used for the impregnation process is shown in Fig. 6. In consists of an impregnation tank and reservoir for the impregnation solution. The vacuum lines permit the transfer of the impregnation solution to and from the impregnation tank. The plaques were mounted on a terminal post at the commencement of the process and inserted in the impregnation tank. The jar was evacuated for 5 min before the impregnation solution was drawn in. The tank was then opened to atmospheric pressure. After a 5-min soak period, the plaques were dried for 2 to 3 hrs at 80°C. They were then immersed into 25% KOH at 80°C.

The KOH solution was open to the atmosphere only during the immersion of the electrode. At all other times, the surface of the solution was blanketed with N_2 to prevent carbonate build-up. After immersion in KOH for 20 min, the plaque was removed and placed into a beaker of distilled water. Subsequently, the plates were thoroughly washed by forcing distilled water through the plaque until the wash water in contact with the plate had a pH of less than 8.0. No loss of active material was observed in this process. The plate was then dried, weighed and the whole process repeated.

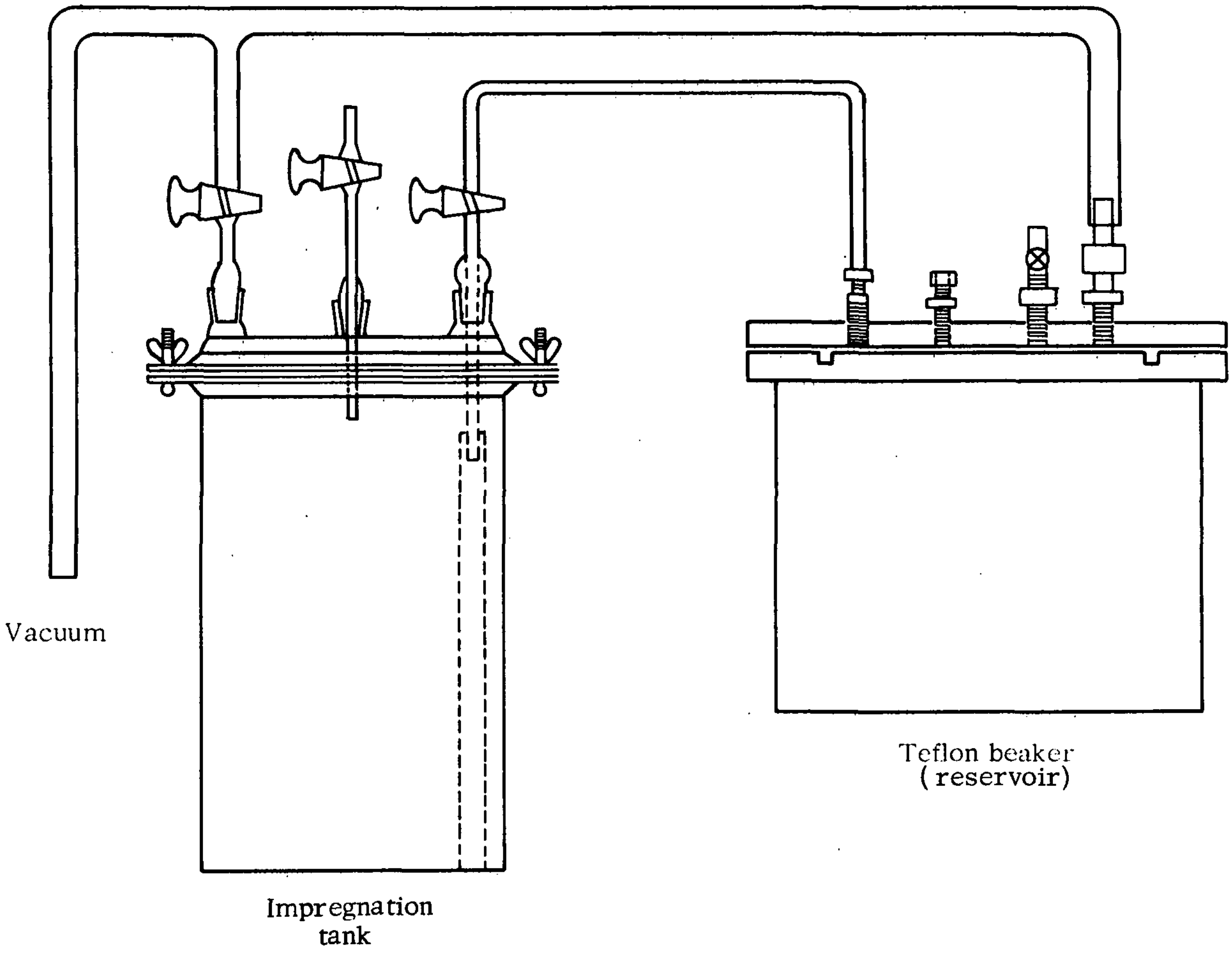

Fig. 6. Vacuum impregnation apparatus

The basic conditions for positive plates were impregnation with saturated nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in water, and conversion in 25% KOH at 80°C. Up to 9 impregnation steps were necessary to obtain the high loading level of positive plates. The prepared electrodes and their characteristics are summarized in Table VI. The values given for the theoretical capacity of positives were calculated from the weight based on the one electron reaction $Ni(OH)_2 \cdot 1/2\ H_2O \rightarrow NiOOH$. In earlier measurements[3] it has been established that the values so calculated correlate well with results obtained by chemical analyses.

For negative plates, a saturated solution was made up from $Cd(NO_3)_2 \cdot 4H_2O$ in water. All other conditions were identical to those of the positive plates. The negative electrode data are summarized in Table VII. Here, only 2 or 3 impregnation steps were necessary to obtain the desired loading level. Due to the higher porosity, a slightly larger weight gain per impregnation step was observed with the loose sintered then with the slurry coated plaques. The theoretical capacities of negative plates were calculated from the weight gain based on $Cd(OH)_2$.

C. Electrochemical Conversion Method

This impregnation method is very similar to the chemical conversion procedure described above; the main difference was that after impregnation the plaque was transferred directly into the KOH solution at 80°C. The terminal post was inserted into a sleeve in the lid of the KOH bath and the necessary cell connections made before immersion so that the cathodic current flows immediately on immersion. The effect of this current is to reduce NO_3^- ions in the plaque structure, ensuring more complete conversion and localizing the deposition within the plaque structure. After immersion in KOH for 20 min, the plate was washed as described above. The conditions for our preparations were that plates were impregnated with a saturated solution prepared from $Ni(NO_3)_2 \cdot 6H_2O$ or $Cd(NO_3)_2 \cdot 4H_2O$ directly followed by conversion in 25% KOH at 80°C with a cathodization current of 150 mA/cm^2 for 20 min. The plates impregnated by the electrochemical conversion process are summarized in Tables VIII and IX.

The values listed for the theoretical capacities were again calculated from the weight gain based on the respective compounds listed above as active materials. For positive plates, the high specific capacity could not be reached even after up to 12 impregnation steps. This number of cycles is greater than that normally required in commercial practice, probably because the extent of plaque corrosion (the corrosion product becomes positive active material) is a great deal less in the preparation considered here. Also, the difference in plate and plaque thickness indicates a significant surface buildup at the highly loaded plates.

The theoretical capacity of negative electrodes was based on $Cd(OH)_2$ as active material. Since a cathodic current is applied during the conversion step, it is possible, however, that part of the active material in negative plates is reduced to Cd. The analysis of plates impregnated by this procedure using selective extractions with Muspratt solution showed that approximately 20 to 50% of the active material is present in the form of Cd rather than $Cd(OH)_2$. Thus, the calculated values for the theoretical capacity might be approximately 3 to 7% too low. For negative plates, 2 or 3 impregnation steps were sufficient to achieve the desired loadings.

D. High Temperature Electrochemical Impregnation Process

1. Background

Electrochemical precipitation of nickel or cadmium hydroxide from solutions of the nitrates is dependent on the cathodic reduction of the nitrate ion to produce a high pH in the immediate environment of the electrode. More particularly, this increase in pH will occur in the pore structure during the reaction of nitrate ion to NO according to:

$$NO_3^- + 2\,H_2O + 3e \rightarrow NO + 4\,OH^-.$$

When the cathodization is carried out with a porous nickel electrode, most of the precipitation will occur within the pore structure. However, good distribution of the active materials in the pore structure is going to be strongly dependent on the rate of generation of hydroxyl ions (i.e., the current density) and the steady-state conditions of the diffusion processes associated with the precipitation reaction. The diffusion processes involved are nickel or cadmium ions diffusing into the pore structure, H^+ ions diffusing into the pore structure, and OH^- ions diffusing into the bulk of the solution from the pores of the electrode. The relative rates of diffusion are obviously important, and since OH^- and H^+ ions have diffusion coefficients that are considerably larger than those of cadmium and nickel, there is need for careful regulation of the pH of the bulk of the solution. At a high rate of OH^- ion production, the ions may diffuse out of the pore structure, precipitating nickel or cadmium hydroxide in the bulk of the solution or on the surface of the plaque. The pH should be maintained at a level where hydroxyl ions diffusing to the surface produce water rather than precipitate the metal hydroxide. However, the hydrogen ion concentration in the bulk should not be high enough for the hydrogen ions to compete with the metal ions in terms of the rate of diffusion into the pore structure of the plaque. In summary, a delicate balance of metal ion concentration, pH, and current density is required to precipitate the hydroxide uniformly throughout the plaque. To some extent, the process is self-regulating in that generation of OH^- ions probably occurs primarily on the bare nickel surface; i.e., once the metal hydroxide is precipitated on the surface, the reaction progresses faster at another site.

Control of current density and metal ion concentration is relatively straightforward, but maintaining pH at a constant level is much more difficult. The anodic process (which would be O_2 evolution in the absence of any other oxidizable species) is generating H^+ ions in solution at the rate of one per electron passing through the cell. At the same time, the hydroxyl ions produced at the cathode are to a large extent precipitated as the metal hydroxide. Since the range of interest is close to pH 4, very rapid changes in the acid direction would be anticipated in the normal volumes of solution used unless specific precautions are taken to control pH. In practice, the pH can be stabilized by adding sodium nitrite to the solution; this prevents undue accumulation of H^+ ions by the following reaction:

$$3\ NaNO_2 + 2\ H^+ + 2\ NO_3^- \rightarrow 3\ NaNO_3 + 2\ NO + H_2O.$$

This probably cannot be regarded as a true buffering reaction since there is no reverse reaction, but it effectively prevents a rapid fall in pH. In the presence of sodium nitrite, the anodic process becomes oxidation of nitrite to nitrate rather than oxygen evolution. This reaction still generates H^+ ions at the same rate according to:

$$NO_2^- + H_2O \rightarrow NO_3^- + 2\ H^+ + 2\ e.$$

Also, it is probable that nitrite contributes to the cathodic reaction, according to:

$$NO_2^- + H_2O + e \rightarrow NO + 2\ OH^-.$$

The relative contributions of nitrate and nitrite in the precipitation of the metal hydroxide are going to depend on the bulk concentrations and the location of the reaction in the pore structure of the nickel plaque.

From the above, it is apparent that the role of NO_2^- is also complex, but probably the concentration level is not critical as long as it exceeds a minimum value necessary to stabilize the pH according to the above equation.

In normal operation, the impregnation bath will become depleted in NO_2^- and Ni^{++} or Cd^{++} and buildup in NO_3^-. If additions of $NaNO_2$ and $Ni(NO_3)_2$ or $Cd(NO_3)_2$ are made to maintain the initial levels, then the bath will become progressively more concentrated in $NaNO_3$. These factors are of lesser importance in a laboratory study when fresh solutions can be used consistently but pose problems for large-scale, long-term operations.

In comparison with the conventional methods of impregnation, the electrochemical process is more complex in terms of operation. However, the number of variables involved should give, under optimum conditions, better control of the distribution and morphology of the active materials. Also, from a practical point of view, plates are produced in a relatively short time (~1 hr) in a one-step process. The prime advantage of operation at high temperatures (the boiling point of the solution) appears to be the opportunity for good pH control and consequently higher specific capacities than have been reported at lower temperatures. The process appears to be equally suitable for the manufacture of positive and negative plates.

A study of the high temperature electrochemical impregnation process was reported earlier.[6] The objective was to define the critical variables of the process and to optimize the conditions of impregnation in terms of uniformity and reproducibility at the highest possible specific capacity.

The most important finding of this study of electrochemical impregnation was that the specific capacity attainable by this process was critically dependent on the physical characteristics of the porous nickel substrate. At the experimental conditions investigated, plaques prepared by a dry sintering technique had better characteristics for the high temperature electrochemical impregnation process than those prepared by slurry coating. The maximum stable capacities measured during these cycling tests were 7.7 Ahr/in.^{3} for a positive plate and 7.4 Ahr/in.^{3} for a negative plate.

The most important physical characteristic for a plaque to have in order to produce a plate of high specific capacity appears to be a high porosity, uniformly distributed through the plaque. In other words, the high porosity must not be due to the presence of large void spaces in the plaque. In addition, the surface structure, especially the pore opening, can be expected to have a major effect on the various diffusion processes involved during the plate preparation. There are indications that the slurry formulation and the coating process used here might cause a slight narrowing of the pore entrance at the plaque surface during preparation. Scanning electron micrographs of the various plaques did not, however, provide conclusive evidence of this. The loose sintered plaque appears to meet the necessary criteria for the high temperature electrochemical impregnation process more readily than the plaque prepared by the slurry-coating procedure. In a brief examination, it was found that the nature of the plaque was not as critically important for the conventional methods of impregnation. It was also demonstrated that plaque corrosion was as little as 3% during the high temperature electrochemical impregnation process. This compares to ~8% in the conventional impregnation methods.

2. Experimental procedure

The solutions were prepared by dissolving the requisite quantities of the hydrated salts of the metal nitrate and sodium nitrite in about half the required amount of water. This solution was then diluted to give the desired concentrations. They were, in this study, 2M $Cd(NO_3)_2$ or 2M $Ni(NO_3)_2$ with 0.3M $NaNO_2$.

Immediately after dilution, the pH of the solution was measured using a pH meter sensitive to better than 0.01 pH units. The solutions were typically just below pH 3 (the actual value depends on the free acid content of the nickel or cadmium nitrate salt). The pH was then adjusted to 4.0 by the addition of dilute sodium hydroxide accompanied by vigorous stirring. (A local sharp increase in pH can precipitate nickel or cadmium hydroxide which does not redissolve.) The solution was then allowed to stand for a period of time not less than overnight. Immediately prior to use, the solution was readjusted to pH 4.0 ± 0.01. The solution was then brought to its boiling point and the impregnation process started as soon as possible.

The plaques were cleaned within a period of 24 hr prior to impregnation by heating in H_2 at 400°C for 15 min. Between cleaning and impregnation, the plaques were stored in plastic containers.

The plaque was mounted vertically in a Teflon jig centrally located between two platinized titanium counterelectrodes. As much as possible of the side walls, end walls, and bottom of the box-like jig was removed to permit free circulation of the electrolyte.

The jig containing the electrodes, previously connected to the power supply but with the current set to the minimum position of the power supply, was lowered into the hot electrolyte. The plaque was thus at a cathodic potential at all times. As soon as the temperature reached its previous value of about 105°C, the power supply was adjusted to provide a constant current of 0.25 A/in.^{2} for negative and 0.5 A/in.^{2} for positive plate impregnation. At the end of the impregnation time the electrode was removed from the electrolyte, immediately immersed in distilled water, and subsequently washed thoroughly in a flowthrough system.

The plates prepared by the high temperature electrochemical impregnation process are listed in Table X and XI. As outlined above, this impregnation process depends on a careful balance of various diffusion processes. Thus, to obtain optimum results it is not only necessary to strictly control the impregnation parameters but also to match the condition to the plaque type (porosity, thickness, etc.). Thus, each plaque would require different impregnation conditions. This was not possible within the scope of this program. Therefore, one set of pre-selected parameters (concentration, current density, etc.) was used to impregnate all plates. All other conditions being equal, the plate loading was initially directly proportional to the impregnation time. Beyond a certain impregnation time, the loading with active material starts to level out and eventually becomes nearly independent of impregnation time. This problem was encountered with positive plates, especially when a high loading with active material was attempted using slurry coated plaque.

Under these conditions a further complication arises, leading to surface buildup of active material, which is reflected in large differences between plaque and plate thickness. No such difficulties were encountered with the impregnations of negative plates.

Table VI. Positive Plates, Chemical Impregnation Process

[Saturated $Ni(NO_3)_2$, 25% KOH, 80°C]

Plate*	Thickness (mil) Plaque	Thickness (mil) Plate	Number of Impregnations	Weight Gain (g/in.^{3})	Theoretical Capacity (Ahr/in.^{3})
619-4-11A 20-D-5	22.4	23.3	5	22.00	6.25
619-4-11 B 20-D-8	21.9	22.7	8	32.56	8.6
619-4-13A 20-D-5	22.2	23.3	5	24.00	6.3
619-4-13B 20-D-8	22.2	23.9	8	34.80	9.1
619-4-1A 30-D-5	31.7	31.9	5	20.43	5.4
619-4-1B 30-D-8	31.6	32.0	8	27.20	7.2
619-4-23A 30-D-5	30.6	34.3	5	20.60	5.3
619-4-23B 30-D-8	30.7	39.7	9	29.65	7.8
598-26-1C A 30-S-5	25.0	26.4	5	18.48	4.9
598-26-1C B 30-S-8	25.6	28.6	9	28.02	7.4
598-25-1A A 30-S-5	27.9	28.8	5	21.35	5.6
598-25-1A B 30-S-8	28.0	29.1	9	29.00	7.6
598-29-1A A 30-P-8	31.6	33.7	9	27.20	7.1
598-36-1A A 20-P-5	23.1	24.6	3	16.20	4.2
598-36-1A B 30-P-5	24.3	24.6	4	16.30	4.3
598-29-1B A 30-P-5	30.1	31.0	3	16.10	4.2
598-29-1B B 30-P-5	30.0	30.2	3	17.10	4.6

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*First line = identification number

Second line = plate code: nominal thickness (mil) - plaque type - nominal loading (Ahr/in.^{3}); D = loose sinter, screen substrate; S = slurry coated; screen substrate; P = slurry-coated, perforated sheet substrate.

Table VII. Negative Plates, Chemical Impregnation Process

[Saturated $Cd(NO_3)_2$, 25% KOH, 80°C]

Plate*	Thickness (mil)		Number of Impregnations	Weight Gain (g/in.^{3})	Theoretical Capacity (Ahr/in.^{3})
	Plaque	Plate			
619-4-18-A 20-D-5	23.5	23.9	2	15.20	5.7
619-4-18-B 20-D-8	23.8	24.1	3	22.35	8.2
619-4-22A 20-D-5	21.8	22.9	2	16.30	6.3
619-4-22-B 20-D-8	21.7	22.6	3	26.55	9.7
619-4-26A 30-D-5	20.6	30.8	2	14.84	5.4
619-4-26B 30-D-8	31.2	31.2	3	23.05	8.4
619-4-28A 30-D-5	38.6	38.7	2	17.85	6.5
619-4-28A 30-D-8	39.0	39.2	3	24.59	9.0
598-26-2A A 30-S-5	26.7	27.9	2	16.30	6.0
598-26-2A B 30-S-8	26.9	27.4	3	25.10	9.2
598-25-1C A 30-S-5	28.1	29.2	2	17.75	6.7
598-25-1C B 30-S-8	28.2	29.0	3	22.88	8.4
598-29-1A B 30-P-8	28.5	28.6	3	24.15	8.8
598-28-1C A 20-P-5	21.4	22.1	2	13.61	5.0
598-28-1C B 20-P-5	24.3	24.4	2	14.22	5.2
598-29-1C A 30-P-5	29.6	29.6	2	15.07	5.5
598-29-1C B 30-P-5	30.2	30.2	2	15.22	5.6

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*First line = identification number

Second line = *plate code: nominal thickness (mil) - plaque type -* nominal loading (Ahr/in.^{3}); D = loose sinter, screen substrate; S = slurry coated; screen substrate; P = slurry-coated, perforated sheet substrate.

Table VIII. Positive Plates, Electrochemical Conversion Process

[Saturated $Ni(NO_3)_2$, 25% KOH, 80°C, 0.15 A/cm^2]

Plate*	Thickness (mil) Plaque	Thickness (mil) Plate	Number of Impregnations	Weight Gain ($g/in.^3$)	Theoretical Capacity ($Ahr/in.^3$)
619-4-39A 20-D-5	21.8	24.5	6	21.28	5.6
619-4-39B 20-D-8	21.5	26.2	12	27.60	7.2
619-4-42A 20-D-8	21.9	25.3	7	27.95	7.3
619-4-42B 20-D-5	22.0	24.4	5	21.60	5.7
619-4-43A 30-D-5	31.2	32.8	4	19.80	5.2
619-4-43B 30-D-5	31.2	33.5	8	28.00	7.4
619-4-44B 30-D-8	28.9	33.3	10	28.30	7.5
598-35-1C A 20-S-5	24.9	26.1	5	17.68	4.7
598-35-1C B 20-S-8	24.6	29.2	10	21.75	5.7
598-35-1B A 20-S-5	24.3	25.7	5	16.77	4.4
598-35-1B B 20-S-8	24.9	29.7	10	22.50	5.9
598-34-1B A 30-S-5	26.9	28.4	5	17.95	4.8
598-34-1B B 30-S-8	26.5	27.5	8	25.80	6.8
598-33-4C A 30-S-5	26.4	27.0	5	18.80	4.9
598-33-4C B 30-S-8	27.9	29.4	10	28.00	7.3
598-34-1D A 30-P-8	33.8	38.8	10	29.70	7.8
598-34-1D B 30-P-5	32.8	35.2	5	18.45	4.8
598-29-1D A 30-P-8	29.8	32.9	9	27.80	7.3
598-29-1D B 30-P-5	29.2	32.7	5	17.82	4.7

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*First line = identification number

Second line = plate code: nominal thickness (mil) - plaque type - nominal loading ($Ahr/in.^3$); D = loose sinter, screen substrate; S = slurry coated; screen substrate; P = slurry-coated, perforated sheet substrate.

Table IX. Negative Plates, Electrochemical Conversion Process

[Saturated $Cd(NO_3)_2$, 25% KOH, 80°C, 0.15 A/cm^2]

Plate *	Thickness (mil) Plaque	Thickness (mil) Plate	Number of Impregnations	Weight Gain ($g/in.^3$)	Theoretical Capacity (Ahr/in^3)
619-4-40-A 30-D-5	21.5	22.6	2	15.12	5.5
619-4-40B 20-D-8	22.5	25.1	4	20.85	7.5
619-4-45A 20-D-5	21.2	22.4	2	16.48	6.0
619-4-45B 20-D-8	21.8	23.1	3	23.27	8.5
619-4-46A 30-D-5	30.3	30.9	2	14.20	5.2
619-4-46B 30-D-8	29.6	30.8	3	20.75	7.6
619-4-47A 30-D-5	31.4	32.2	2	15.72	5.7
619-4-47B 30-D-8	31.4	33.1	3	22.30	8.2
598-35-1A A 20-S-5	25.0	25.4	2	13.83	5.1
598-35-1A B 20-S-8	24.2	24.7	3	19.67	7.2
598-35-2A A 20-S-5	25.5	25.6	2	13.40	4.9
598-35-2A B 20-S-8	25.3	26.2	3	20.20	7.4
598-33-4B A 30-S-5	27.3	28.2	2	13.42	4.9
598-33-4B B 30-S-8	26.8	27.0	3	21.30	7.8
598-33-4D A 30-S-5	28.1	28.2	2	13.98	5.1
598-34-1A A 30-P-5	32.8	33.9	2	13.50	4.9
598-34-1A B 30-P-8	31.5	33.9	3	24.20	8.8

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*First line = identification number

Second line = plate code: nominal thickness (mil) - plaque type - nominal loading ($Ahr/in.^3$); D = loose sinter, screen substrate; S = slurry coated; screen substrate; P = slurry-coated, perforated sheet substrate.

Table X. Positive Plates, High Temperature Electrochemical Impregnation

[2 M $Ni(NO_3)_2$, 0.3 M $NaNO_2$, pH 4, 104°C, 0.5 A/in.^{2}]

Plate*	Thickness (mil)		Impregnation Time (min)	Weight Gain (g/in.^{3})	Theoretical Capacity (Ahr/in.^{3})
	Plaque	Plate			
619-4-23 A 20-D-5	22.3	35.4	127	21.30	5.6
619-4-23 B 20-D-8	21.5	22.9	75	24.50	6.4
619-4-24 A 20-D-5	22.1	22.7	60	15.50	4.1
619-4-24 B 20-D-8	21.5	24.7	120	20.50	5.4
619-4-29 A 30-D-5	35.1	35.5	40	15.48	4.1
619-4-29 B 30-D-8	35.9	42.2	60	33.20	8.7
619-4-31 A 30-D-5	36.7	39.3	120	23.80	6.2
619-4-31 B 30-D-8	36.7	46.3	240	28.30	7.4
598-32-1C A 20-S-5	24.3	25.5	60	21.05	5.8
598-32-1C B 20-S-8	24.7	34.6	100	17.70	4.6
598-32-1B A 20-S-5	24.6	30.5	150	23.40	6.1
598-32-1B B 20-S-8	25.1	26.8	120	24.70	6.5
598-34-1A A 30-S-5	26.9	37.1	120	24.20	6.3
598-34-1A B 30-S-8	26.9	37.8	180	22.92	6.0
598-34-1D A 30-S-5	26.8	29.1	120	24.40	6.4
598-34-1D B 30-S-8	26.5	38.6	180	23.78	6.2
598-26-1C A 20-P-5	25.6	25.9	60	21.00	5.5

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*First line = identification number

Second line = plate code: nominal thickness (mil) - plaque type - nominal loading (Ahr/in.^{3}) ; D = loose sinter, screen substrate; S = slurry coated; screen substrate; P = slurry-coated, perforated sheet substrate.

Table X. (continued)

Plate*	Thickness (mil) Plaque	 Plate	Impregnation Time (min)	Weight Gain (g/in.^{3})	Theoretical Capacity (Ahr/in.^{3})
598-26-1C B 20-P-8	26.1	30.9	120	24.20	6.4
598-27-1C A 20-P-5	23.0	24.6	60	21.60	5.7
598-27-1C B 20-P-8	23.4	24.7	75	20.92	5.5
598-33-3C A 30-P-5	27.3	29.0	105	26.20	6.9
598-33-3C B 30-P-8	27.3	29.9	120	25.18	6.6
598-33-3D A 30-P-5	27.8	28.7	60	22.55	5.9
598-33-3D B 30-P-8	28.5	32.2	120	25.45	6.7

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*First line = identification number

Second line = plate code: nominal thickness (mil) - plaque type - nominal loading (Ahr/in.^{3}) ; D = loose sinter, screen substrate; S = slurry coated; screen substrate; P = slurry-coated, perforated sheet substrate.

Table XL Negative Plates, High Temperature Electrochemical Impregnation

[2 M $Cd(NO_3)_2$, 0.3 M $NaNO_2$, pH 4, 104°C, 0.25 A/in.^{2}]

Plate*	Thickness (mil) Plaque	Thickness (mil) Plate	Impregnation Time (min)	Weight Gain (g/in.^{3})	Theoretical Capacity (Ahr/in.^{3})
619-4-21 A 20-D-5	21.5	22.6	5	14.70	5.4
619-4-21 B 20-D-8	21.9	23.7	13	22.38	8.2
619-4-37 A 20-D-5	24.5	24.5	10	18.90	6.9
619-4-37 B 20-D-8	25.0	26.0	20	23.08	8.5
619-4-33 A 30-D-5	32.1	32.6	10	14.20	5.2
619-4-33 B 30-D-8	31.7	37.0	20	19.50	7.2
619-4-34 A 30-D-5	31.0	32.0	60	19.80	7.3
619-4-34 B 30-D-8	30.9	41.4	40	21.00	7.7
598-32-1A A 20-S-5	24.9	25.3	10	12.70	4.7
598-32-1A B 20-S-8	25.3	26.9	20	22.80	8.4
598-33-4A A 30-S-5	28.0	28.0	10	10.70	3.9
598-33-4A B 30-S-8	27.2	27.5	20	26.00	9.5
598-34-1C A 30-S-5	26.8	26.8	15	13.10	4.8
598-34-1C B 30-S-8	26.7	27.8	60	20.40	7.5
598-27-1A A 20-P-5	22.1	22.5	10	13.90	5.1
598-27-1A B 20-P-8	21.9	25.4	15	20.10	7.4
598-27-2C A 20-P-5	23.1	23.5	15	16.10	5.9
598-27-2C B 20-P-8	22.8	23.0	30	23.70	8.7

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*First line = identification number

Second line = plate code: nominal thickness (mil) - plaque type - nominal loading (Ahr/in.^{3}); D = loose sinter, screen substrate; S = slurry coated; screen substrate; P = slurry-coated, perforated sheet substrate.

Table XL (continued)

Plate*	Thickness (mil)		Impregnation Time (min)	Weight Gain (g/in.^{3})	Theoretical Capacity (Ahr/in.^{3})
	Plaque	Plate			
598-33-3A A 30-P-5	28.8	29.0	10	14.70	5.4
598-33-3A B 30-P-8	28.3	29.6	15	19.70	7.2
598-33-3B A 30-P-5	29.0	29.0	10	14.60	5.4
598-33-3B B 30-P-8	28.6	33.5	20	18.60	6.8
619-4-48 A 20-S-5	24.6	24.7	13	11.15	4.1
619-4-48-B 20-S-8	23.7	25.8	34	11.03	4.0

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*First line = identification number

Second line = plate code: nominal thickness (mil) - plaque type - nominal loading (Ahr/in.^{3}); D = loose sinter, screen substrate; S = slurry coated; screen substrate; P = slurry-coated, perforated sheet substrate.

VI. PLATE TESTING FOR MANUFACTURING VARIABLES

A. Test Procedure

The comparative testing for all electrodes consisted of a simulated near-earth orbit cycle regime at a charge/discharge rate corresponding to a 60 min/30 min cycle at a 25% depth of discharge and 5% overcharge. All plates were subjected to 100 cycles. The testing was carried out in flooded medium with two oversized counterelectrodes. The electrodes were cycled in batches of 20 electrodes using all 20 stations of the NASA battery formation cycler (EMR, Inc., Model No. BF-300). The recorded parameters were: (1) capacity after formation, (2) charge and discharge potentials during cycling, (3) capacity after 100 cycles, (4) capacity limits between which the cycling occurred, and (5) physical changes (weight loss, shedding, etc.). A total of 120 electrodes were tested. The detailed experimental procedure was as follows:

1. A test plate was assembled in a cell with two overdesigned counterelectrodes in 20% KOH.

2. The plate was formed by a minimum of six full cycles at the 2-hr rate with 100% overcharge. The last three cycles were recorded and the capacity of the formed plate was determined.

3. The formed plate was scrubbed to remove loosely-adherent surface material, washed, dried, and weighed.

4. All electrodes of a test set were adjusted to an approximately equal capacity by clipping off an appropriate (weighed) amount of the plates with higher capacity. This was done in order to cycle all plates at the same current and equal rate.

5. The cell was reassembled using 30% KOH. A reference electrode (charged negative plate) was also included in each cell to allow for accurate potential measurements.

6. The plate capacity was measured at the C/2 rate by a full discharge after charging with 100% overcharge.

7. The plates were cycled (60/30 min cycles, 25% depth of discharge, 5% overcharge), starting with the discharge portion of the cycle, from 80% state-of-charge for negative plates and 100% state-of-charge for positive plates. The cycling was carried out at room temperature for 100 cycles.

8. After the last charge the plate was completely discharged (0.8 V cell potential) at the C/2 rate to determine the charge left in the plate after 100 cycles.

9. The plate was fully charged (100% overcharge) and the capacity determined again (C/2 rate).

10. At the end of testing the electrodes were inspected, washed, dried, weighed, and stored in plastic bags (Scotchpak, 3 M).

B. Results and Discussion

1. Positive plates

a. Potential data

Typical test cycles for positive electrodes cycling between various state-of-charge limits are shown in Figs. 7, 8, and 9. The shape of the potential time curves remained practically unchanged throughout the 100 test cycles. The comparison of the 5th and the 99th cycle showed no differences. Figs. 7, 8, and 9 also contain potential time curves of the final discharge, the following extensive charge (overcharge), and the subsequent discharge. Significant differences were observed between the potential data of the 30/60 min test cycles (25% depth of discharge) and the final discharge after overcharge. In the latter case the initial potential decrease was more rapid followed by a long, fairly flat plateau. From the difference in capacity between the final discharge and the discharge after 100% overcharge, we can determine the limits of the state-of-charge between which the electrodes actually cycled. Initially, all positive electrodes started the cycle regime in the fully-charged state. However, at the end of the test period, positive electrodes typically cycled between 35 and 60% state-of-charge. This indicates that the 5% overcharge during each cycle at the rate and temperature of the test was not sufficient to compensate for the charge inefficiency due to oxygen evolution, which is a parasitic reaction throughout the major part of the positive plate charging. The rate of oxygen evolution increases with increasing state-of-charge. Thus, the cycled capacity moves to lower state-of-charge until the excess charge input during each cycle is equivalent to the amount of oxygen generated. Measurements of the rate of oxygen evolution on positive plates as a function of the state-of-charge showed that at room temperature NiO_x electrodes begin to evolve oxygen at approximately 15% state-of-charge.[10] From these quantitative measurements one can calculate that the state-of-charge at which the oxygen evolution is equivalent to the amount of overcharge (5% of the C/4 rate) is approximately 60%. This correlates very well with observed values of 50 to 75%. It might be noted here that electrodes 598-33-1AA (Fig. 7), which finally cycled between 25 and 50% state-of-charge, started from the completely discharged state with a charge cycle (it had accidentally discharged completely during an early test cycle).

A closer comparison of the various discharge curves shows several additional features of interest. The shape and potential region of the 30-min discharge is relatively similar to the initial section of the full discharge after overcharge, even though the actual cycling occurs in the middle section of the total plate capacity.

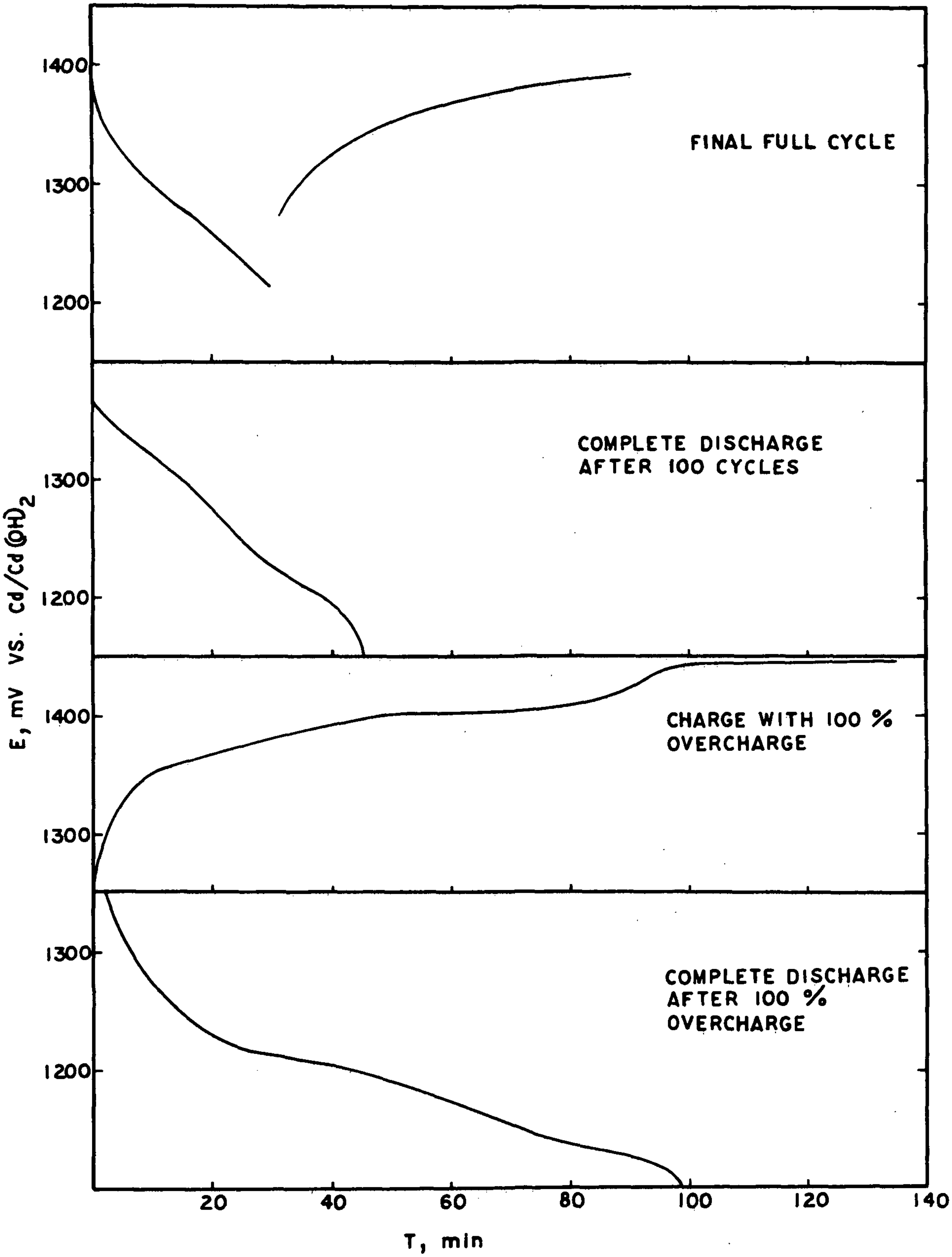

Fig. 7. Typical potential-time curves during test cycling of positive plates (598-33-1AA, 20-S-5 H. T. electrochemical impregnation); room temperature, 30% KOH

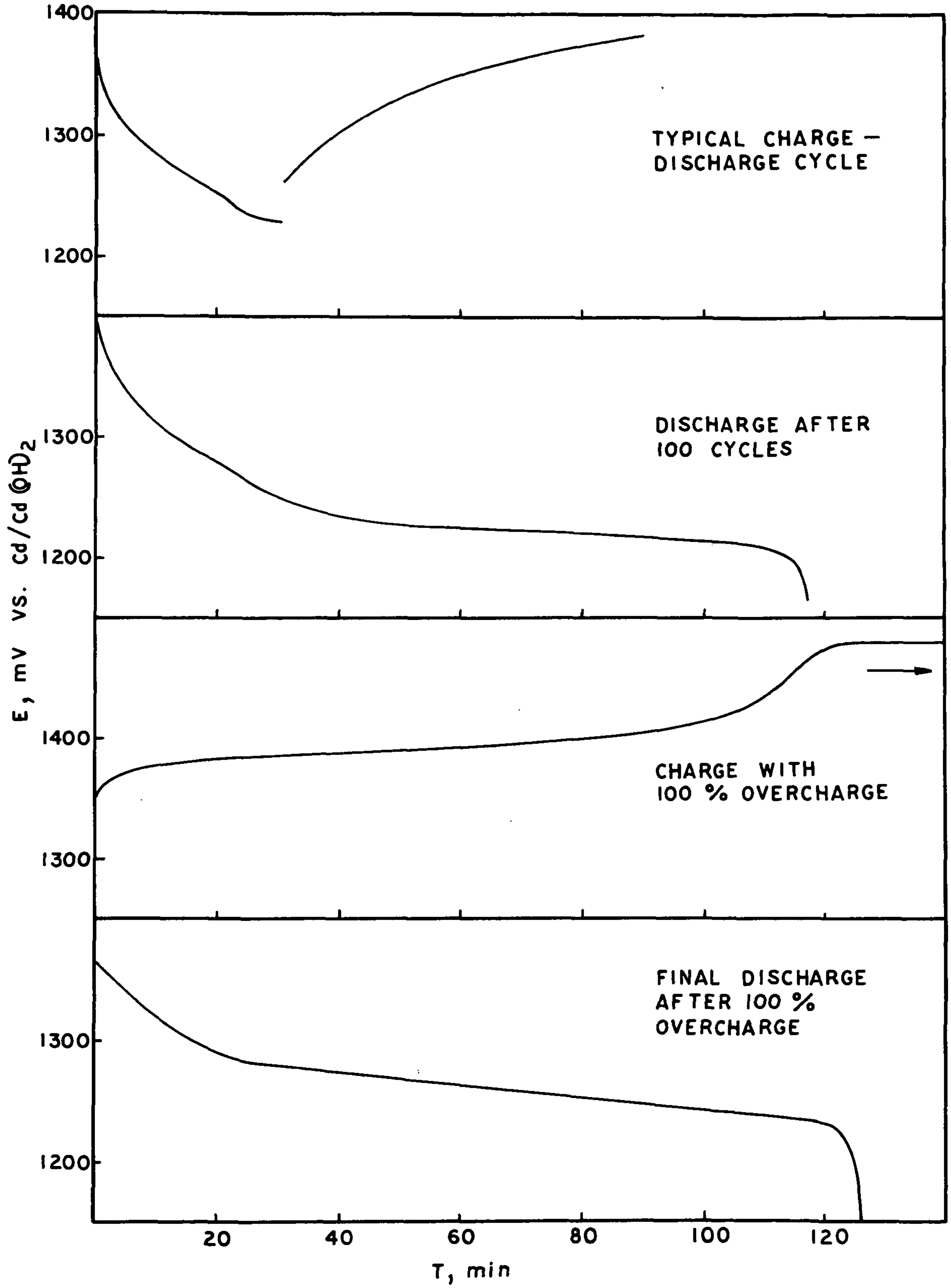

Fig. 8. Typical potential-time curves during test cycling of positive plates (619-4-39A, 20-D-5, electrochemical conversion); room temperature, 30% KOH

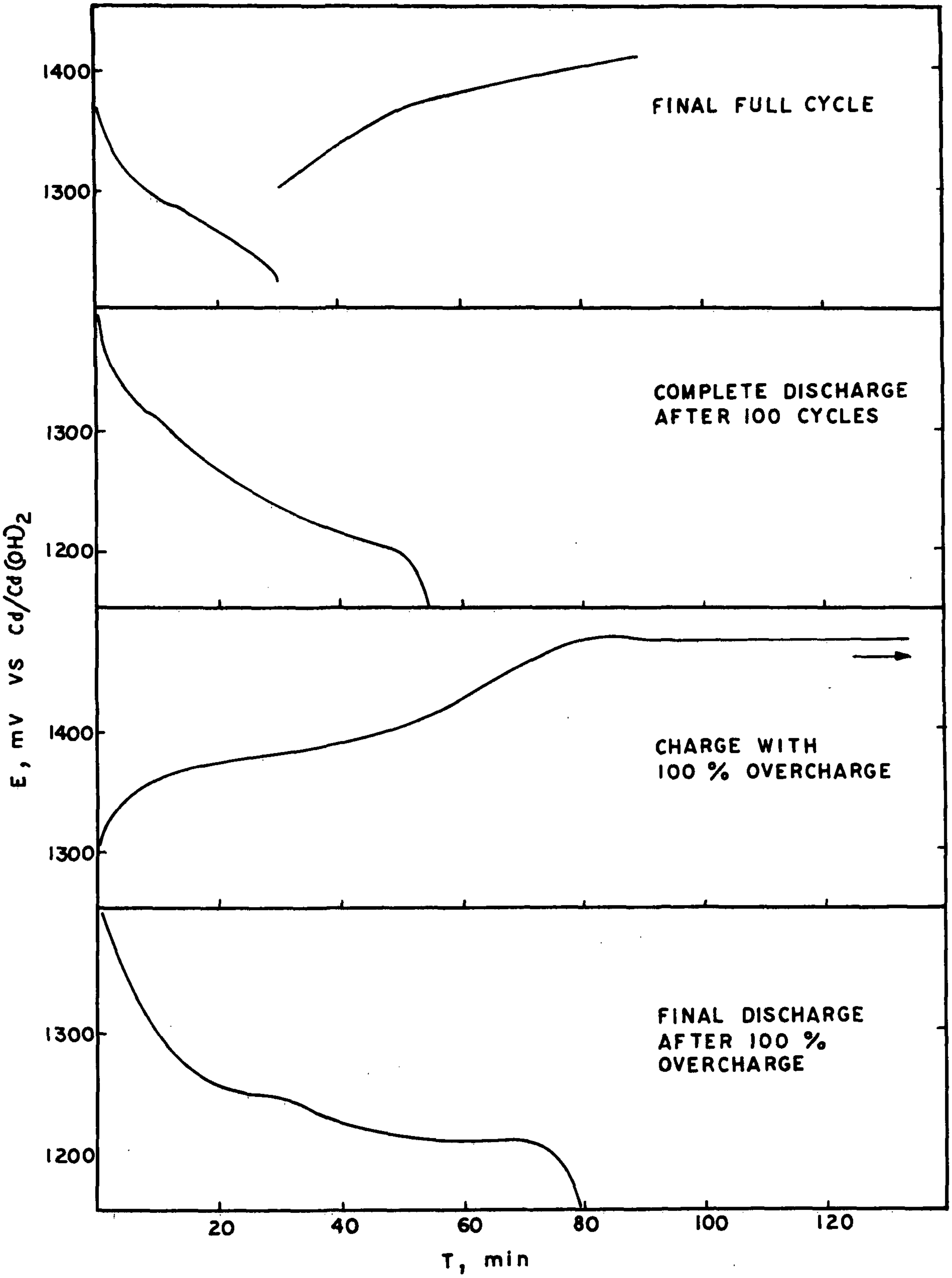

Fig. 9. Typical potential-time curves during test cycling of positive plates (593-32-1C, 20-S-5, H. T. electrochemical impregnation); room temperature, 30% KOH

On total discharge a potential step was observed after 30 min (e.g., Fig. 7) corresponding to the end of the regular test cycle discharge. In the discharge following 100% overcharge, this potential step can still be noticed at the same state of charge. A similar but smaller discontinuity could also be observed in the potential upon charging after the first complete discharge. The initial part of the charging curve (from 0 to 50 min in Fig. 7) follows the same pattern as the charging curve during the test cycling (shown in the upper part of the figure). However, at the time where the charge input is equal to the previous discharge (at 50 min in Fig. 7), a decreased rate of change in electrode potential was observed until the potential rise due to oxygen evolution occurred. In the case of plate 598-32-1C (Fig. 9) this feature of the charging curve is overshadowed by the potential increase close to full charge. Thus, the potential-time behavior of a positive plate cycled extensively between limits equivalent of 25% of its capacity appears to be quite similar to that of a nearly full-cycled electrode.

b. Capacity data

The capacity data, specifically the overall capacity change (formation and test cycling), and the capacity change during the 100 test cycles as a percent value are listed in Table XII. The last column gives the final plate capacity as obtained by a discharge at the C/2 rate after 100% overcharge as a percent value of the theoretical capacity. The preceding column contains the percent value of the capacity retained during the test cycling. It is obtained by dividing the final capacity × 100 by the capacity after formation (i.e., prior to the 30/60 min test cycling).

The data is arranged according to the standard order of the treatment combinations in a factorial design, as shown in Table I. Here we have two factors at three levels and two factors at two levels. As discussed earlier, Yates' method of analysis applies only to two level factorials. The data therefore was analyzed as a combination of several two level factorials of the form shown in Table II.

All in all, nine two-level factorial combinations can be written. They were analyzed using a computer program based on Yates' evaluation method described in detail in Appendix A. For this analysis a full set of data is necessary, and thus a few values had to be estimated. They were determined in two ways: (1) by an estimate based on the neighboring values and the general trends, and (2) as an average of the measured values of the two level factorial to be evaluated. The second method results in complete neutral values. Both procedures led to the same conclusions.

The limits of significance were calculated on the basis that third and higher order interactions can be regarded as error. The comparison of the data was carried out for two levels of confidence: 95% and 80%. The resulting conclusions are summarized in Table XIII and XIV and are further explained in the following paragraphs. The individual computer printouts are included in Appendix B.

Even without factorial analysis, it can be seen from the experimental data that no large differences exist between the various positive plates, and the systematic capacity changes

Table XII. Postive Plate Capacity Data During 100 Test Cycles

	Treatment Combination	**Plate ***	Thickness (mils)	Theoretical Capacity (Ahr/in.^{3})	% of Capacity retained after 100 cycles	Final Capacity % of Theoretical
CHEMICAL CONVERSION	1	**619-4-11A** **619-4-13A** **20-D-5**	23.3 23.3	6.25 6.30	83 97	87 94
	b	**619-4-1A** **619-4-23A** **30-D-5**	31.9 34.3	5.37 5.27	98 100	112 104
	a_1	**20-S-5**				
	a_1b	**598-26-1**C A **598-25-1**A A **30-S-5**	26.4 28.8	4.86 5.61	97 68	99 69
	a_2	**598-36-1A** A **598-36-1A** B **20-P-5**	24.6 24.6	4.24 4.28	106 110	105 107
	a_2b	**598-29-1B** A **598-29-1B** B **30-P-5**	31.0 30.2	4.24 4.65	100 104	81 91
	d	**619-4-11B** **619-4-13B** **20-D-8**	22.7 23.9	8.55 9.14	89 97	76 87
	bd	**619-4-1B** **619-4-23B** **30-D-8**	32.0 39.7	7.16 7.80	99 100	96 66
	a_1d	**20-S-8**				
	a_1bd	**598-26-1C** B **598-25-1A** B **30-S-8**	28.6 29.1	7.38 7.62	96 100	84 93
	a_2d	**20-P-8**				
	a_2bd	**598-29-1A** A **30-P-8**	33.7	7.13	91	97
ELECTROCHEMICAL CONVERSION	c_1	**619-4-39A** **619-4-42B** **20-D-5**	24.5 24.4	5.57 5.67	100 90	68 88
	bc_1	**619-4-43A** **619-4-44A** **30-D-5**	32.8 31.9	5.18 4.65	98 96	99 79
	a_1c_1	**598-35-1C** A **598-35-1B** A **20-S-5**	26.1 25.7	4.65 4.40	115 97	97 88
	a_1bc_1	**598-34-1B** A **598-33-4C** A **30-S-5**	28.4 27.0	4.75 4.93	86 93	83 86
	a_2c_1	**20-P-5**				
	a_2bc_1	**598-34-1D** B 598-29-1D B 30-P-5	35.2 32.1	4.80 4.67	113 116	128 104

Table XII. (Continued)

	Treatment Combination	Plate *	Thickness (mils)	Theoretical Capacity (Ahr/in.^{3})	% of Capacity retained after 100 cycles	Final Capacity % of Theoretical
ELECTROCHEMICAL CONVERSION	c_1d	619-4-39B 619-4-42A 20-D-8	26.2 25.3	7.23 7.32	96 94	79 89
	bc_1d	619-4-43B 619-4-44B 30-D-8	33.5 33.3	7.35 7.53	107 104	85 76
	a_1c_1d	598-35-1C B 598-35-1B B 20-S-8	29.2 29.7	5.70 5.88	106 97	84 75
	a_1bc_1d	598-34-1B B 598-33-4C B 30-S-8	27.5 29.4	6.75 7.34	100 98	79 80
	a_2c_1d	20-P-8				
	a_2bc_1d	598-34-1D A 598-29-1D A 30-P-8	38.8 32.9	7.78 7.28	112 75	82 56
HIGH TEMPERATURE ELECTROCHEMICAL IMPREGNATION	c_2	619-4-23A 619-4-24A 20-D-5	35.4 22.7	5.58 4.06	95 80	63 78
	bc_2	619-4-29A 619-4-31A 30-D-5	35.5 39.3	4.05 6.22	95 89	72 96
	a_1c_2	598-32-1C A 598-32-1B A 20-S-5	25.5 30.5	5.80 6.12	99 100	96 76
	a_1bc_2	598-34-1A A 598-34-1D A 30-S-5	37.1 29.1	6.33 6.40	83 70	69 84
	a_2c_2	598-26-1C A 598-27-1C A 20-P-5	25.9 24.6	5.50 5.65	66 105	73 85
	a_2bc_2	598-33-3C A 598-33-3D A 30-P-5	29.0 28.7	6.85 5.92	84 83	95 80
	c_2d	619-4-23B 619-4-24B 20-D-8	22.9 24.7	6.42 5.37	81 104	89 90
	bc_2d	619-4-29B 619-4-31B 30-D-8	42.2 46.3	8.70 7.42	109 93	56 67
	a_1c_2d	598-32-1C B 598-32-1B B 20-S-8	34.6 26.8	4.60 6.46	100 87	64 87
	a_1bdc_2	598-34-1A B 598-34-1D B 30-S-8	37.8 38.6	6.00 6.23	88 83	67 74
	a_2c_2d	598-26-1C B 598-27-1C B 20-P-8	30.9 24.7	6.35 5.47	78 100	79 67
	a_2bc_2d	598-33-3C B 598-33-3D B 30-P-8	29.9 32.2	6.59 6.66	84 91	92 83

Table XIII. Positive Plates – Conclusions from the Factorial Evaluation of the Capacity Retained During 100 Test Cycles

No.	Block	Confidence Limits	
		95%	80%
1	$C_0\ C_1/A_1\ A_2$	—	- interaction plaque – loading (P plaque less change)
2	$C_0\ C_1/A_0\ A_2$	—	thick plate less change low loading less change - interaction plaque - loading
3	$C_0\ C_1/A_0\ A_1$	—	electrochem conv. less change high loading less change + interaction plaque – thickness + interaction thickness – loading
4	$C_0\ C_2/A_0\ A_1$	+ interaction plaque – thickness	D plaque less change high loading less change + interaction thickness - impreg. - interaction thickness – loading
5	$C_0\ C_2/A_0\ A_2$	chem. conv. less change + interaction plaque – thickness + interaction plaque – impreg. + interaction plaque – loading - interaction impreg. – loading	——
6	$C_0\ C_2/A_1\ A_2$	—	chem. conv. less change thin plate less change
7	$C_1\ C_2/A_1\ A_2$	electrochem. conv. less change	- interaction plaque – thickness
8	$C_1\ C_2/A_0\ A_2$	—	electrochem. conv. less change thick plate less change
9	$C_1\ C_2/A_0\ A_1$	electrochem. conv. less change high loading less change + interaction plaque – thickness - interaction thickness – loading	thin plate less change (D plaque less change) + interaction plaque – impreg.

Table XIV. Positive Plates – Conclusions from the Factorial Evaluation of the Final Capacity as Fraction of the Theoretical Capacity

No.	Block	Confidence Limits 95%	80%
1	C_0 C_1/A_1 A_2	—	low loading less change
2	C_0 C_1/A_0 A_2	—	low loading less change
3	C_0 C_1/A_0 A_1	—	low loading less change
4	C_0 C_2/A_0 A_1	—	low loading less change chem. conv. less change
5	C_0 C_2/A_0 A_2	—	chem. conv. less change
6	C_0 C_2/A_1 A_2	chem. conv. less change	low loading less change
7	C_1 C_2/A_1 A_2	—	low loading less change + interaction plaque type – thickness
8	C_1 C_2/A_0 A_2	—	low loading less change - interaction thickness – loading
9	C_1 C_2/A_0 A_1	—	electrochem. conv. less change

during the 100 test cycles were very small. The statistical evaluation showed that the positive plates prepared by the electrochemical and chemical conversion methods retained, on the average, a larger fraction of their capacity than the plates prepared by the high temperature electrochemical impregnation process. This is not surprising in view of the relatively heavy surface buildup of active material on the latter plates. The functioning of the high temperature electrochemical impregnation process is based on a delicate balance of several diffusion processes, and thus special impregnation conditions are required for the different plaques. This was discussed in some detail in the section describing the plate manufacture. Within the constraints of this program it was, however, not possible to determine the optimum impregnation conditions for each plaque. It is interesting to note that blocks No. 4 and 9 (Table XIII), both of which contain plates prepared from loose-sintered and slurry-coated plaques on screen substrate impregnated by the high temperature electrochemical process, show the plates from loose-sintered plaques to retain a larger fraction of their capacity. Since this difference does not appear when comparing the chemical and electrochemical conversion process (block 3), it has to be ascribed to the high temperature electrochemical impregnation process. This is in agreement with our earlier findings that the dry sintered plaques were more suitable for this impregnation process than our slurry coated plaque material. This is probably due to a more open surface of the loose powder sinters and to an increased porosity.

The comparison of slurry-coated material on screen or perforated strip substrate favors the perforated strip substrate. We also observed significant interaction between plaque type and loading and/or thickness. In block No. 1, for example, the notation " -interaction plaque-loading" means that the effect on capacity retention of a change in plaque type (S or P plaque) is larger at the lower loading. The conclusion that the plaque type is of larger importance at the lower loading appeared to be more general. In the blocks containing dry sintered plaque impregnated by the high temperature electrochemical method (blocks 4 and 9), the effect of changing the plaque type was larger on the thick plates and with the high temperature electrochemical impregnation method.

The comparison of the final capacity with the theoretical capacity leads to the same results as obtained above with respect to the impregnation process, however the differences between the various impregnation methods are much less pronounced. The only other significant factor is the loading level. The percent of capacity decrease is smaller at the lower loading.

c. Physical changes

The physical inspection of the various positive plates showed some characteristic differences. The highly loaded plates fabricated by the chemical conversion method had a relatively low mechanical strength, and at the highly loaded loose sinters some disintegration of the plaque structure was observed. This was a consequence of plaque corrosion during the large number of consecutive impregnation steps. As one would expect, this effect was most apparent with the loose sintered plaque which had the highest porosity. Highly loaded plates prepared by the electrochemical conversion process were moderately buckled and showed some surface cracks. With highly loaded plates using perforated nickel strip as substrate, a separation of the plaque from the substrate along part of the outside edges was observed in some instances. The plates with low loading, prepared by either of the two conversion processes, were of good appearance.

All plates prepared by the high temperature electrochemical impregnation process were of good appearance and showed practically no buckling. As mentioned earlier, plates of slurry-coated plaques for which high loadings were attempted showed considerable surface buildup of active material. In general the surface material was removed by the scrubbing after formation. This removal was also reflected in a decreased plate thickness, especially in those cases where excessive increases were observed following impregnation.

The changes described above occurred mainly during the formation period. During the actual test cycling, the weight loss of the plates was very small and no systematic trend could be determined. The measured weight changes of the plates were between 0.01 and 0.1g. If one assumes as the worst case that the whole weight loss was in the form of active material, only a 1 to 3% change in capacity could result.

2. Negative plates

a. Potential data

Typical potential-time curves of negative plates during the 30/60 min test cycling are shown in Figs. 10 and 11. The discharge curves were quite flat and no significant changes could be observed during the cycling. For example, the shape of the 5th and 99th discharges were practically identical. Also, a comparison of the different plates did not show any characteristic variations.

As mentioned before, the cycle testing was started with a discharge cycle of the plates which had been previously charged to 80% of their full capacity. Besides the reduction of some oxygen which was evolved as a side reaction at the counter electrodes and, at least in part, diffused through the separator to the negative plates, no parasitic reactions occurred. Thus, since the charge input was 5% in excess of the capacity extracted during discharge, the state-of-charge limits between which the electrode cycled moved towards higher values. At the end of the 100 test cycles, most negative plates showed potential-time curves upon charge similar to the one shown in Fig. 10. The potential shift to more cathodic values towards the end of the charge cycle is due to the beginning of hydrogen evolution.

Figs. 10 and 11 also contain the potential-time curves of the complete discharge after 100 cycles and the discharge after the subsequent extensive charging (100% overcharge). Upon discharge beyond the regular 30-min cycle, a small more or less pronounced potential shift to more anodic values can be seen. This shift is, however, smaller than those observed at positive plates. After extensive charge the potential plateau was quite flat without indication of any memory effects.

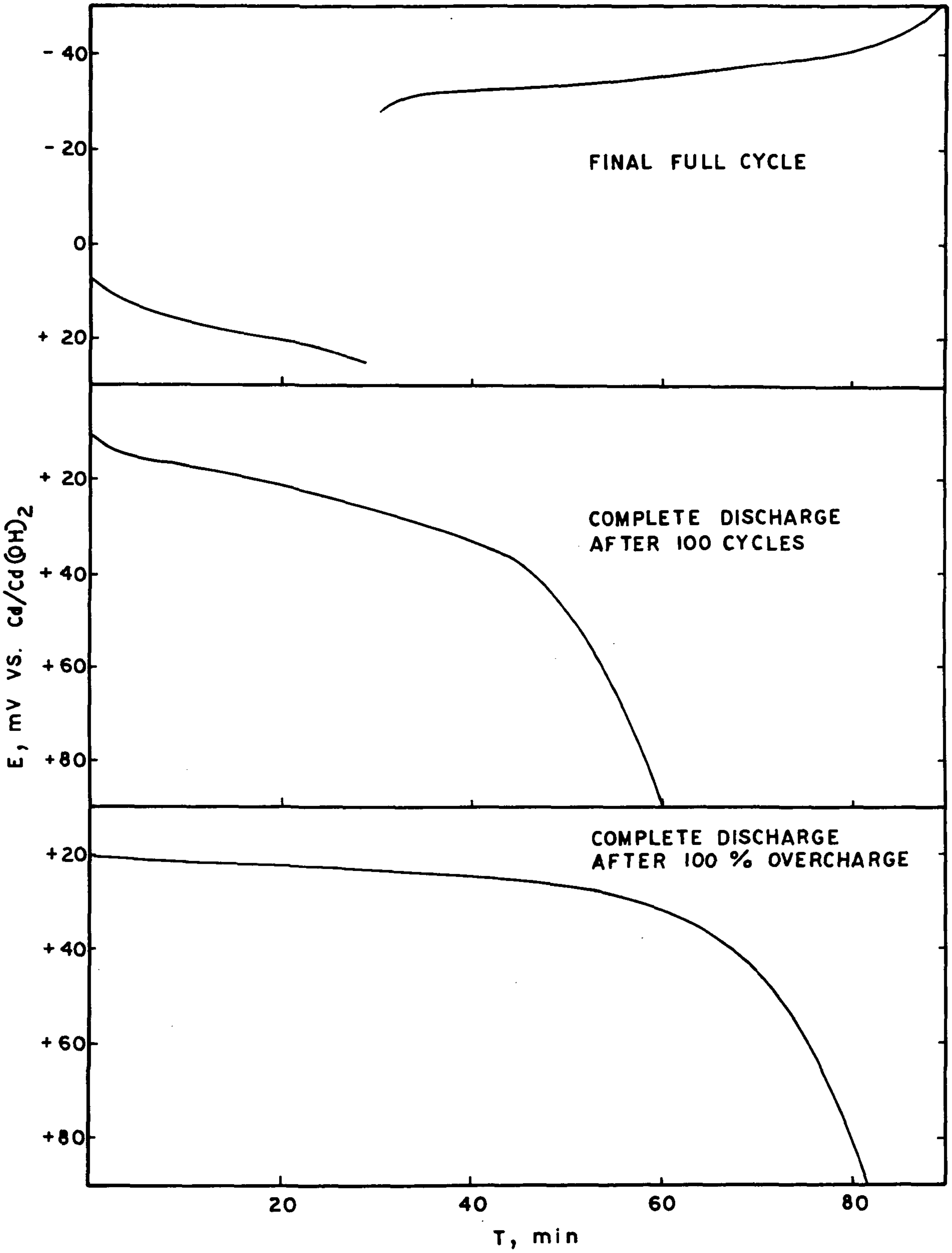

Fig. 10. Typical potential-time curves during test cycling of negative plates (619-4-26B, 30-D-8, chemical conversion); room temperature, 30% KOH

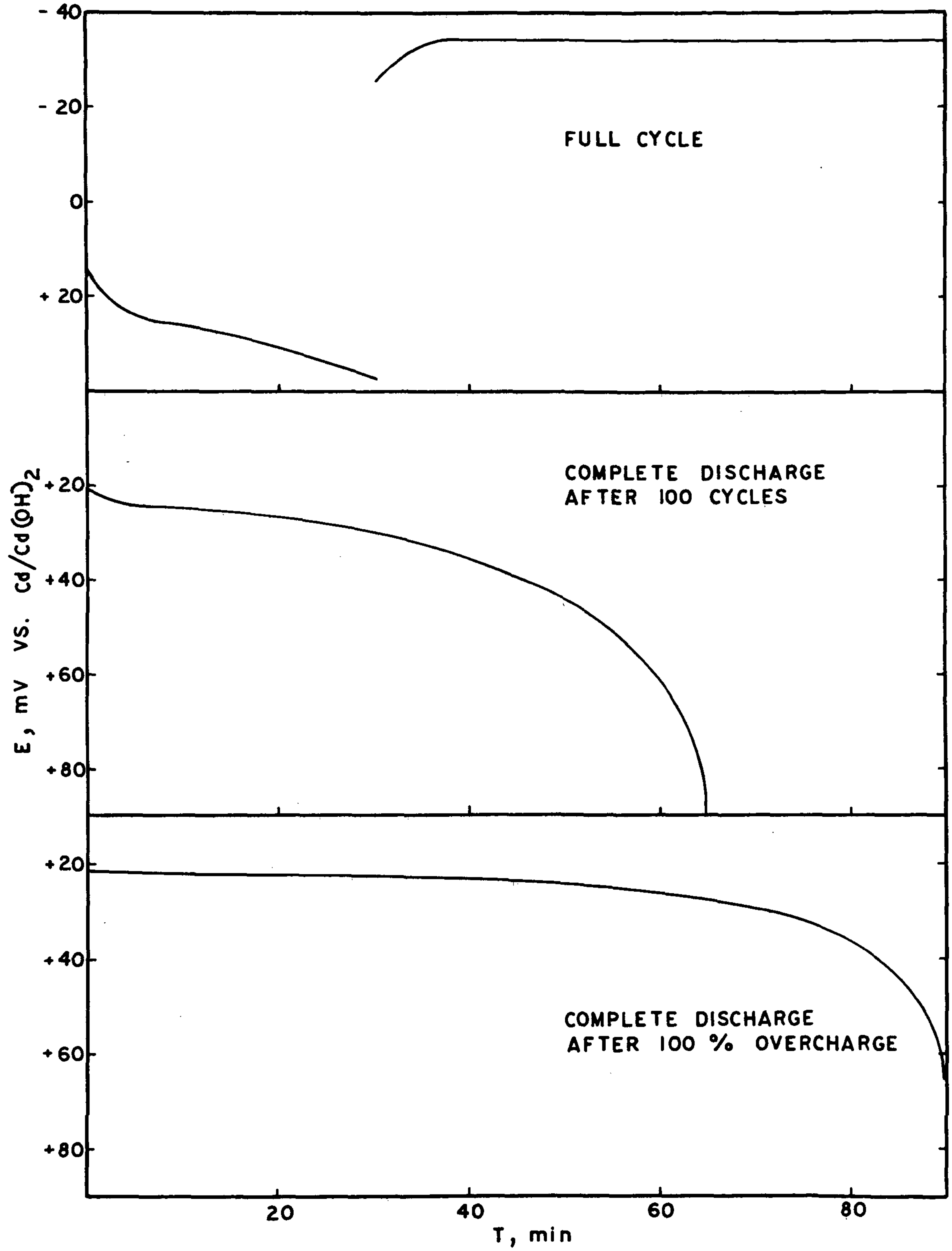

Fig. 11. Typical potential-time curves during test cycling of negative plates (598-34-1C, 30-S-8, H. T. electrochemical); room temperature, 30% KOH

b. Capacity data

The capacity data for negative plates are summarized in Table XV. Here again, as in the table for positive plates, the last column gives the final plate capacity as obtained by a discharge at the C/2 rate after 100% overcharge as a percent of the theoretical capacity. The preceding column contains the percent value of the capacity retained during the 100 test cycles. It is defined by final capacity × 100 capacity prior to test cycling. The data is again arranged in standard order of a factorial design as shown in Table I.

The analysis was again carried out in blocks of nine 2-level factorials as discussed above for positive plates. The individual computer printouts are included in the Appendix B. The conclusions are summarized for the two levels of confidence (95 and 80%) in Tables XVI and XVII. With negative plates the capacity changes were significantly larger than those observed with positive plates. The best results, that is, the smallest capacity changes during the test cycling were observed at plates impregnated by the high temperature electrochemical impregnation process. The performance of plates impregnated by either of the two conversion processes appears to depend on the plaque type, with slurry-coated plaque on screen favoring the chemical conversion process and loose-sintered plaque favoring the electrochemical conversion method.

Of the three plaque types, the slurry coated material on perforated nickel substrate showed the best overall performance. This applied to all impregnation methods. The loose sintered material performed the poorest of the three types. This result might indicate that a lower plaque porosity is favorable for the capacity retention of negative plates.

Another general result was that the plates with lower loading retain a larger fraction of their capacity during cycling. The thinner plaque was more favorable, especially in the comparison involving the high temperature electrochemical impregnation method and loose sintered plaque (blocks 4 and 9, Table XVI).

The results show also a number of significant interactions between plaque type, plaque thickness, impregnation method, and loading. For example, the -interaction between thickness and impregnation method (Table XVI, No. 1) means that the effect due to the variation in thickness is smaller at plates produced by the electrochemical conversion method than by the chemical conversion method. Thus, we find that the effect due to the variation in thickness is most pronounced in plaques produced by the high temperature electrochemical impregnation process followed by the chemical and electrochemical conversion methods. In the same way we find that the effect of changing the plaque type is larger for the chemical and electrochemical conversion processes than for the high temperature electrochemical impregnation process.

From these results one would expect a negative plate fabricated from a thin, slurry-coated plaque on a perforated substrate and impregnated by the high temperature electrochemical method to a low loading level to show the smallest capacity change during cycling at the indicated test regime.

The statistical analysis of the overall capacity changes (formation and test cycling) leads to the same conclusions.

Table XV. Negative Plate Capacity Data During 100 Test Cycles

	Treatment Combination	Plate *	Thickness (mils)	Theoretical Capacity (Ahr/in.^{3})	% of Capacity retained after 100 cycles	Final Capacity % of Theoretical
CHEMICAL CONVERSION	1	619-4-18A 619-4-22A 20-D-5	23.9 22.9	5.67 6.26	72 87	60 69
	b	619-4-26A 619-4-28A 30-D-5	30.8 38.7	5.43 6.50	77 76	59 60
	a_1	20-S-5				
	a_1b	598-26-2A A 598-25-1C A 30-S-5	27.9 29.2	5.96 6.71	81 86	64 49
	a_2	598-28-1C A 598-28-1C B 20-P-5	22.1 24.4	4.97 5.20	81 118	81 99
	a_2b	598-29-1C A 598-29-1C B 30-P-5	29.6 30.2	5.52 5.57	80 90	56 68
	d	619-4-18B 619-4-22B 20-D-8	24.1 22.6	8.15 9.70	74	50
	bd	619-4-26B 619-4-28B 30-D-8	31.2 39.2	8.42 9.00	68 80	48 62
	a_1d	20-S-8				
	a_1bd	598-26-2A B 598-25-1C B 30-S-8	27.4 29.0	9.15 8.39	79 85	54 60
	a_2d	20-P-8				
	a_2bd	598-29-1A B 30-P-8	28.6	8.84	84	66
ELECTROCHEMICAL CONV.	c_1	619-4-40A 619-4-45A 20-D-5	22.6 22.4	5.50 6.02	73 83	36 55
	bc_1	619-4-46A 619-4-47A 30-D-5	30.9 32.2	5.19 5.75	81 85	56 59
	a_1c_1	598-35-1A A 598-35-2A A 20-S-5	25.4 25.6	5.06 4.89	79 76	53 52
	a_1bc_1	598-33-4B A 598-33-4D A 30-S-5	28.2 28.2	4.92 5.12	82 86	52 51

Table XV. (Continued)

	Treatment Combination	Plate*	Thickness (mils)	Theoretical Capacity (Ahr/in^3)	% of Capacity retained after 100 cycles	Final Capacity % of Theoretical
ELECTROCHEMICAL CONVERSION	a_2c_1	20-P-5				
	a_2bc_1	598-34-1A A	33.9	4.94	91	66
		30-P-5				
	dc_1	619-4-40B	25.1	7.50	67	47
		619-4-45B	23.1	8.52	90	63
		20-D-8				
	bdc_1	619-4-46B	30.8	7.59	82	55
		619-4-47B	33.1	8.16	78	56
		30-D-8				
	a_1dc_1	598-35-1A B	24.7	7.20	79	60
		598-35-2A B	26.2	7.38	77	51
		20-S-8				
	a_1bdc_1	598-33-4B B	27.0	7.78	66	51
		30-S-8				
	a_2dc_1	20-P-8				
	a_2bdc_1	598-34-1A B	33.9	8.85	90	44
		30-P-8				
HIGH TEMPERATURE ELECTROCHEMICAL IMPREGNATION	c_2	619-4-21A	22.6	5.40	86	55
		619-4-37A	24.5	6.91	96	70
		20-D-5				
	bc_2	619-4-33A	32.6	5.20	79	46
		619-4-34A	32.0	7.25	99	70
		30-D-5				
	a_1c_2	598-32-1A A	25.3	4.67	103	82
		619-4-48A	24.7	4.09	81	70
		20-S-5				
	a_1bc_2	598-33-4A A	28.0	3.94	90	68
		598-34-1C A	26.8	4.80	89	67
		30-S-5				
	a_2c_2	598-27-1A A	22.5	5.11	98	62
		598-27-2C A	23.5	5.90	87	74
		20-P-5				
	a_2bc_2	598-33-3A A	29.0	5.40	92	71
		598-33-3B A	29.0	5.37	95	76
		30-P-5				
	dc_2	619-4-21B	23.7	8.18	90	64
		619-4-37B	26.0	8.45	96	67
		20-D-8				
	bdc_2	619-4-33B	37.0	7.17	70	41
		619-4-34B	41.4	7.69	89	47
		30-D-8				

Table XV. (Continued)

	Treatment Combination	Plate*	Thickness (mils)	Theoretical Capacity Ahr/in^3	% of Capacity retained after 100 cycles	Final Capacity % of Theoretical
HIGH TEMP. ELECTROCHEM.	a_1dc_2	598-32-1A B 619-4-48B 20-S-8	26.9 25.8	8.35 4.00	90 90	56 72
	a_1bdc_2	598-33-4A B 598-34-1C B 30-S-8	27.5 27.8	9.54 7.47	82 84	56 67
	a_2dc_2	598-27-1A B 598-27-2C B 20-P-8	25.4 23.0	7.39 8.70	70 83	37 57
	a_2bdc_2	598-33-3A B 598-33-3B B 30-P-8	29.6 33.5	7.22 6.83	89 96	60 57

---

*First line = identification number

Second line = plate code: nominal thickness (mil) - plaque type - nominal loading (Ahr/in.^{3}); D = loose sinter, screen substrate; S = slurry coated; screen substrate; P = slurry-coated, perforated sheet substrate.

Table XVI. Negative Plates – Conclusions from the Factorial Evaluation of the Capacity Retained During 100 Test Cycles

	Block	Confidence Limits	
		95%	80%
1	C_0 C_1/A_1 A_2	—	chem. conv. less change P plaque less change low loading less change
2	C_0 C_1/A_0 A_2	P plaque less change	electrochem. conv. less change low loading less change - interaction thickness – impreg.
3	C_0 C_1/A_0 A_1	—	lower loading less change
4	C_0 C_2/A_0 A_1	HT electrochem. temp. less change S plaque less change thin plaque less change low loading less change	- interaction plaque – impreg. + interaction thickness – impreg.
5	C_0 C_2/A_0 A_2	—	P less change HT electrochem. temp. less change low loading less change - interaction plaque – impreg.
6	C_0 C_2/A_1 A_2	—	low loading less change
7	C_1 C_2/A_1 A_2	—	P plaque less change HT electrochem. temp. less change low loading less change - interaction plaque – impreg.
8	C_1 C_2/A_0 A_2	—	P plaque less change - interaction plaque – impreg.
9	C_1 C_2/A_0 A_1	HT electrochem. temp. less change	thin plaque less change low loading less change + interaction thickness – impreg. + interaction thickness – loading

Table XVII. Negative Plates – Conclusions from the Factorial Evaluation of the Final Capacity as Fraction of the Theoretical Capacity

No.	Block	Confidence Limits 95%	Confidence Limits 80%
1	C_0 C_1/A_1 A_2	—	chem. conv. less change thin plaque less change P plaque less change low loading less change - interaction thickness – impreg.
2	C_0 C_1/A_0 A_2	chem. conv. less change P plaque less change	low loading less change - interaction plaque – thickness - interaction thickness – impreg.
3	C_0 C_1/A_0 A_1	chem. conv. less change	thin plaque less change - interaction thickness – impreg. - interaction plaque – thickness
4	C_0 C_2/A_0 A_1	thin plaque less change	S plaque less change low loading less change
5	C_0 C_2/A_0 A_2	—	P less change low loading less change
6	C_0 C_2/A_1 A_2	low loading less change - interaction plaque – impreg. - interaction thickness – impreg.	thin plaque less change - interaction thickness – loading
7	C_1 C_2/A_1 A_2	HT electrochem. temp. less change low loading less change - interaction impreg. – loading - interaction plaque – impreg.	+ interaction plaque – thickness
8	C_1 C_2/A_0 A_2	—	low loading less change - interaction plaque – loading
9	C_1 C_2/A_0 A_1	HT electrochem. temp. less change	S plaque less change thin plaque less change + interaction plaque – impreg. + interaction thickness – impreg. - interaction impreg. – loading

c. Physical changes

The physical inspection of the various negative plates showed no significant differences. All plates, independent of plaque type or impregnation method, had a very good smooth grey appearance. Some loose sintered plates impregnated by the electrochemical conversion method may show a slight inclination to buckling. The weight loss during the test cycling was insignificant per plate. Assuming that the whole weight loss was due to loss of active material (worst case), an average 2% change in capacity would result.

VII. PLATE TESTING FOR OPERATIONAL VARIABLES

A. Test Procedures

This study was intended to examine the effect of various charge (C/20, C/6, and C/2) and discharge (C/5, C, and 5C) rates on differently prepared electrodes. (See factorial design, Table III.) Electrodes, both positives and negatives, of the following types were prepared and tested:

1. Thin slurry-coated plaque on perforated sheet substrate impregnated to a low loading by the chemical conversion method.
2. Thick slurry-coated plaque on perforated sheet substrate impregnated to a high loading by the chemical conversion method.
3. Thick loose sinter plaque on screen impregnated to a high loading by the electrochemical conversion method.
4. Thin slurry-coated plaque on screen impregnated to a low loading by the high temperature electrochemical impregnation method.
5. Thick loose-sintered plaque on screen impregnated to a low loading by the high temperature electrochemical impregnation method.

The characteristics of the various positive and negative plates are summarized in Tables XVIII and XIX. The methods of preparation and the experimental conditions were identical to those used to prepare the plates for the test of manufacturing variables. The plates were formed in 30% KOH @C/2 rate for six cycles with 100% overcharge. After formation they were scrubbed, washed, dried, and cut to obtain two practically identical test plates of each type. The size of the plates was further adjusted to result in test electrodes of nearly identical delivered capacity. This allowed for simultaneously test cycling all twenty test plates (each electrode type was tested in duplicate) with a constant current test cycle. The average plate size was approximately 2 $in.^2$. In order to guarantee a uniform current distribution, the substrate material was exposed along the entire upper edge of the plate and a nickel strip spot welded to it from both sides. Each cell was assembled with two overdesigned counter-electrodes and a negative plate reference electrode. The temperature of all cells was controlled to 20 ± 0.5°C by a thermostatted water bath. The tests were conducted completely flooded in 30% KOH.

We found that the behavior on charge of a given plate was dependent only on the rate of charge and on the rate of discharge directly preceding the charge. This required the starting of each new condition with the discharge of the desired value. Thus, in most cases two full cycles were conducted at each condition. To determine any possible trend in electrode capacity the test sequence was as follows: a_2b_2, a_2b_2, a_1b_2, b_2, a_2b_2, a_2b_1, a_2b_1, ab_1, b_1, a_2, a_2, a, 1, a_2b_2, a_2b_2. (Compare factorial design in Table III). The identical cycles of the combination a_2b_2 (C/2 charge, 5C discharge) would prove the absence of any continuous changes in plate capacity during the time of the complete test.

At each combination, the overcharge for negative plates was approximately 10 to 20% and for positive plates 40%. The discharge was carried out to a voltage cutoff of 0.9V.

B. Results and Discussion

Positive and negative plates of the five electrode types mentioned above were cycled in duplicate. For each combination of charge and discharge rate, the potential was recorded and the delivered capacity determined. Typical examples of an a_1b_2 cycle (C/6 charge, 5C discharge) for a negative and positive plate are shown in Figs. 12 and 13. The capacity data are summarized in Tables XX and XXI. The values given are averages of the two identical plates. An analysis of the data for main effects and interactions showed the following. For positive plates the delivered capacity decreases with a decrease in charge rate and an increase in discharge rate. Thus, the largest capacities were found after charge at the C/2 rate and discharge at the C/5 rate and the smallest at the C/20 charge and 5C discharge rate combination. No significant interactions between charge and discharge rates were detected. A comparison of the relative effects of charge and discharge rate for the five electrode types tested showed no significant differences. The variations were relatively small and regarded within the error limits. (A statistical determination of error was not possible with only one duplicate measurement). The average charge and discharge effects were approximately 5% of the average capacity.

For negative plates the delivered capacity increased with a decrease in charge and discharge rate. Again, no large differences between the various electrodes were detected. The average charge effect was 6% while the average discharge effect was approximately twice as large ($\sim$13% of the average capacity). Here, too, the interaction between the charge and discharge effects were small.

The potentials of positive and negative plates in the half charged state are listed in Tables XXII and XXIII. The values are given for the high and low rate and cover a full order of magnitude for charge and discharge. The potentials listed are averages of duplicate tests. They are not corrected for the ohmic potential drop in the electrolyte. However, since all cells were assembled identically, they can be compared directly. An ideal positive plate should show a low charge and a high discharge potential. If we analyze the data according to this criteria, we find the most favorable potential characteristics exhibited by the loose-sintered plaque impregnated by the electrochemical conversion method and by the high temperature electrochemical impregnation process. Distinctly less favorable was the highly loaded plaque prepared by the chemical conversion process. These same trends in the potential data were also observed during the test cycling to determine the effect of the manufacturing variables. The rate sensitivity of the various types of plates, e.g., in the potential difference between the low and high discharge rates, followed the same previously observed pattern. A further analysis of the influence and interaction between plaque and impregnation method is not possible here.

The best performance of negative plates with respect to electrode potential was obtained with slurry-coated plaques impregnated by the high temperature electrochemical process. The highest polarizations were observed, with the highly loaded plates prepared by the chemical conversion process. These findings agree well with the conclusions drawn from the evaluation of the factorial experiment.

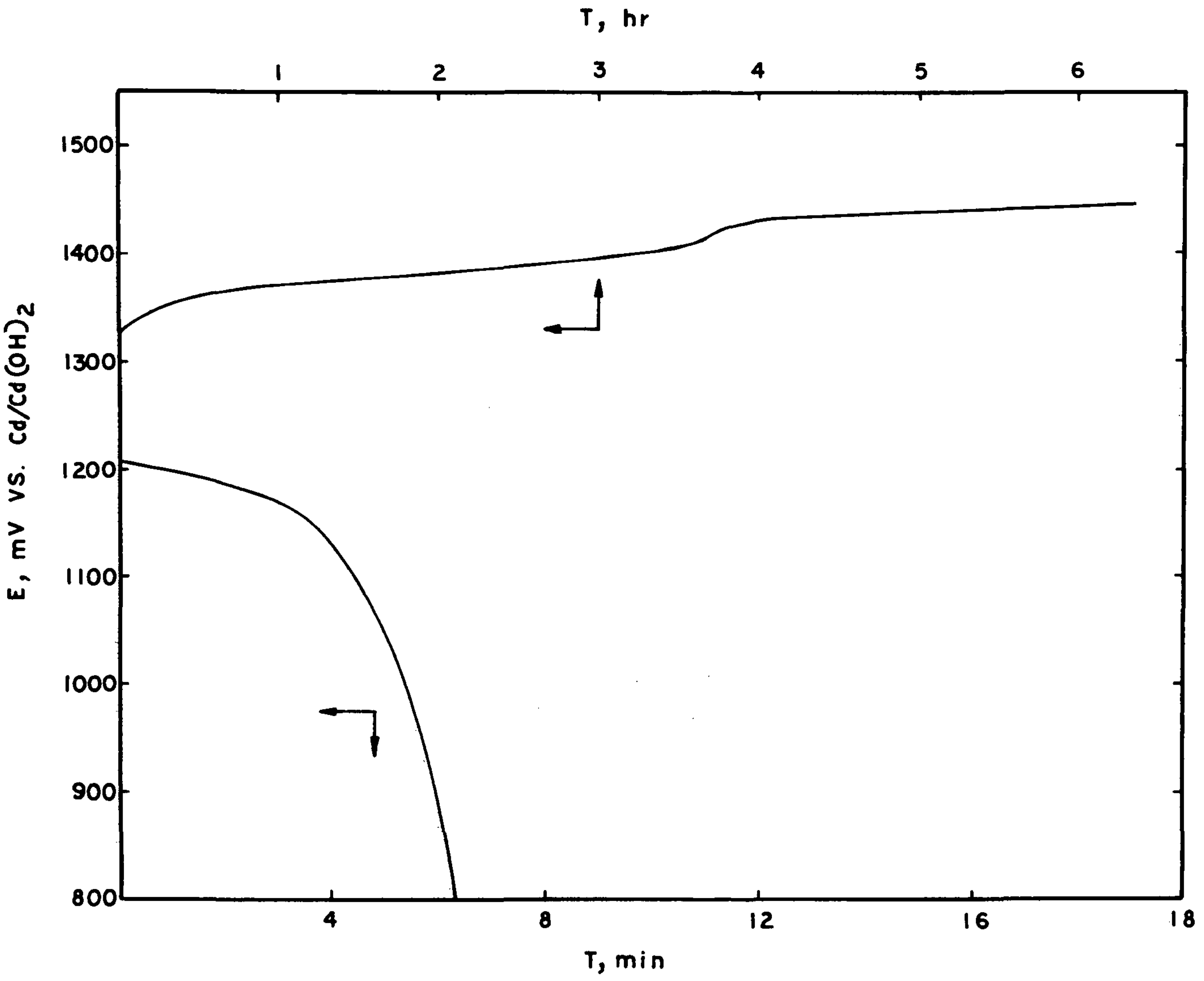

Fig. 12. Typical charge-discharge cycle of a positive plate (598-36-3A) C/6 charge, 5C discharge, 20°C, 30% KOH

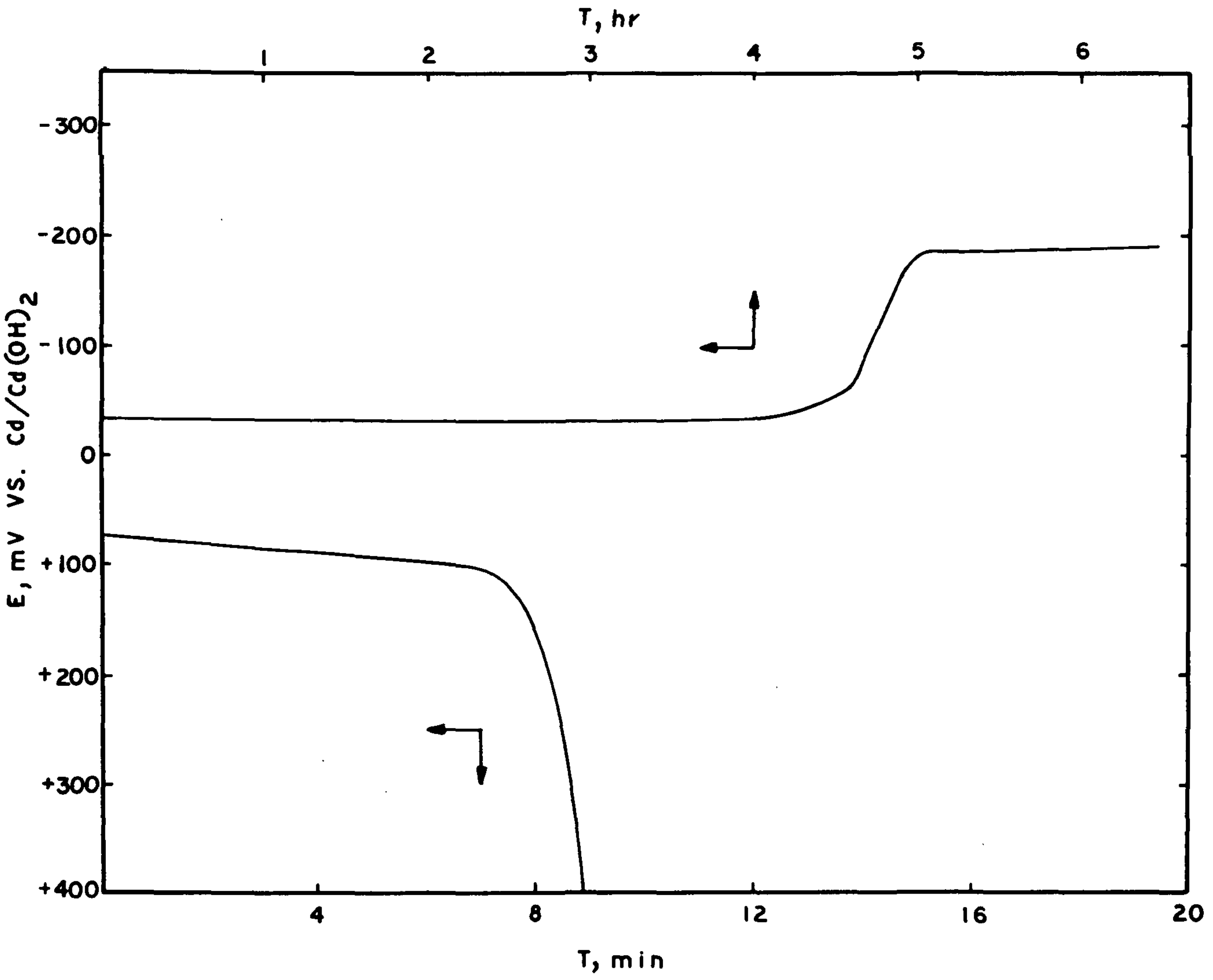

Fig. 13. Typical charge-discharge cycle of a negative plate (598-36-3A) C/6 charge, 5C discharge, 20°C, 30% KOH

Table XVIII. Positive Electrode Data Operational Variables

Plate Identification	Impregnation Method	Thickness (mils)			Impregnation		Wt Gain (g/in.^{2})	Capacity (Ahr/in.^{3})	
		Plaque	Plate	Plate After Form	Time (min)	Steps		Theoretical	After Formation
598-34-2D 30-P-8	Chemical conversion	31.6	35.1	35.2	—	13	1.025	7.65	7.04
598-36-3A 20-P-5		21.8	27.4	27.2	—	6	.444	4.35	5.06
619-4-50A 30-D-8	Electrochemical conversion	30.8	31.4	31.2	—	9	.772	7.20	7.02
598-35-3A 20-S-5	High temperature Electrochemical	22.7	30.7	28.6	125	—	.537	4.58	5.68
619-4-51A 30-D-5		31.8	33.2	32.9	40	—	.641	5.15	5.70

Table XIX. Negative Electrode Data Operational Variables

Plate Identification	Impregnation Method	Thickness (mils)			Impregnation		Wt Gain (g/in.^{2})	Capacity (Ahr/in.^{3})	
		Plaque	Plate	Plate After Form	Time (min)	Steps		Theoretical	After Formation
598-34-2C 30-P-8	Chemical conversion	31.6	35.0	34.8	—	4	.780	8.18	5.54
598-36-3A 20-P-5		22.0	25.0	23.8	—	2	.329	4.78	4.26
619-4-50B 30-D-8	Electrochemical conversion	31.2	33.2	31.5	—	3	.762	8.39	6.90
598-35-1D 20-S-5	High temperature Electrochemical	23.3	24.7	24.9	11	–	.349	5.17	4.54
619-4-51B 30-D-5		32.2	33.2	32.6	10	–	.405	4.48	3.10

Table XX. Delivered Capacity of Positive Plates at Various Charge and Discharge Rates

Treatment Combination	Capacity in mAhr				
	Chemical Conversion		Electrochemical Conversion	High Temperature Electrochemical Impregnation	
	598-36-3A 20-P-5	598-34-2D 30-P-8	619-4-50A 30-D-8	598-35-3A 20-S-5	619-4-51A 30-D-5
1	167	175	142	130	117
a_1	175	190	140	135	130
a_2	195	205	165	155	150
b_1	160	175	115	120	110
a_1b_1	155	170	145	130	125
a_2b_1	140	145	140	115	115
b_2	141	130	101	105	95
a_1b_2	160	140	147	112	105
a_2b_2	180	159	180	147	147

Table XXI. Delivered Capacity of Negative Plates at Various Charge and Discharge Rates

Treatment Combination	Capacity in mAhr				
	Chemical Conversion		Electrochemical Conversion	High Temperature Electrochemical Impregnation	
	598-36-3A 20-P-5	598-34-2C 30-P-8	619-4-50B 30-D-8	598-35-1D 20-S-5	619-4-51B 30-D-5
1	270	248	168	330	193
a_1	280	245	185	300	240
a_2	290	290	190	310	265
b_1	305	270	150	280	270
a_1b_1	260	265	150	250	220
a_2b_1	155	115	160	175	160
b_2	225	98	160	220	144
a_1b_2	212	120	160	180	160
a_2b_2	190	129	190	202	145

Table XXII. Positive Plate Potential Versus Cd/Cd(OH)$_2$*
for Various Charge and Discharge Rates

Impregnation Method	Plate Identification	E (V)				Rating
		Charge Rate		Discharge Rate		
		C/20	C/2	C/5	5C	
Chemical Conversion	598-36-3A 20-P-5	1.389	1.380	1.253	1.122	3
	598-34-2D 30-P-8	1.394	1.426	1.250	1.062	5
Electrochemical Conversion	619-4-50A 30-D-8	1.310	1.406	1.252	1.147	1
High Temperature Electrochemical	598-35-3A 20-S-5	1.384	1.397	1.253	1.106	4
	619-4-51A 30-D-5	1.340	1.393	1.273	1.129	2

* not iR connected

Table XXIII. Negative Plate Potentials Versus Cd/Cd(OH$_2$)*
for Various Charge and Discharge Rates

Impregnation Method	Plate Identification	E (V)				Rating
		Charge Rate		Discharge Rate		
		C/20	C/2	C/5	5C	
Chemical Conversion	598-36-3A 20-P-5	-0.029	-0.045	+0.012	+0.075	2
	598-34-2C 30-P-8	-0.028	-0.084	+0.023 (cell)	+0.265	5
Electrochemical Conversion	619-4-50B 30-D-8	-0.027	-0.071	+0.031	+0.173	4
High Temperature Electrochemical	598-35-1D 20-S-5	-0.022	-0.053	+0.007	+0.076	1
	619-4-51B 30-D-5	-0.019	-0.047	+0.012	+0.085	3

* not iR corrected

VIII. SUMMARY AND CONCLUSIONS

An extensive factorially-designed experiment has been undertaken aimed at illuminating, in a comparative study, the effect of plaque preparation, plaque thickness, impregnation process, and loading level with active material. In evaluating the results the separation of the treatment comparison into main effects and interactions is a convenient and powerful method of analysis, especially in cases where interactions are small relative to main effects. In our case interactions were often found large relative to the main effects, and this demonstrates further the complexity of the problem. The test parameter on which all conclusions for manufacturing variables were based was the capacity change during a specific cycle regime. It was a simulated near earth orbit with a 30-min discharge to 25% depth and a 60-min charge with 5% overcharge.

During the 100 test cycles, overall capacity changes of positive plates and especially the differences between the various plates were very small. The interpretation of the data was further complicated by small main effects and large interactions. Plates prepared by the high temperature electrochemical impregnation of slurry-coated plaque (at the conditions used) were found to show a surface buildup of active material. They also retained slightly less of their capacity during cycling compared to other plate preparations. It appears not justified, however, to attribute this difference to the impregnation process as such since it is so dependent on the proper plaque structure. Initially, positive electrodes cycled between 75 and 100% state-of-charge. Due to oxygen evolution, which is a side reaction during the major part of the charging process, positive plates finally cycled approximately between 35 and 60% state-of-charge. Despite this the plate potential changed significantly during the regular discharge cycle (~150 mV). Characteristic memory effects were observed in potential-time curves. The physical integrity of most plates was good. Only the loose-sintered plaque, highly loaded with active material by the chemical conversion method, showed a substantial weakening of the plaque structure due to corrosion.

The test cycling of negative plates resulted in larger overall capacity changes and in larger differences between the various electrode preparations. The highest capacity retention was obtained with plates prepared by the high temperature electrochemical impregnation process. The superior performance of this impregnation technique may result from a more uniform deposition of the active material in the plaque structure. Plaque type and loading were also of importance with the slurry-coated plaques (lower porosity) and the lower loading levels showing the smaller fractional change in capacity. Here, too, significant interactions were observed between the various parameters. For example, the effect of a change in plaque type was dependent on the impregnation process. It was larger for the conversion methods than for the high temperature electrochemical impregnation process. At negative plates, memory effects were insignificant. The physical properties and the appearance of all plates was very good.

The effect of various charge and discharge rates covering a full order of magnitude was also investigated for a selected group of differently-prepared positive and negative plates. The highest delivered capacities of positive plates were obtained at high charge and low discharge rates. The charge and discharge effects were approximately 5% of the average capacity. With the various positive electrode preparations, only small differences were observed regarding the effect of charge and discharge rate on capacity.

Negative electrodes delivered higher capacities at low charge and discharge rates. Again, the differences between the various preparations were small. The charge and discharge effects were approximately 6 and 13% of the average capacity, respectively.

The charge and discharge potentials for positive and negative plates showed distinct differences for the various preparations. They were more pronounced for negative plates. The smallest polarization of negatives was observed with slurry-coated plaques impregnated by the high temperature electrochemical process. Plates highly loaded by chemical conversion showed the highest polarization on charge and discharge.

Based on the results of this investigation, we may draw the following conclusions: acceptable positive plate can be obtained by any of the three impregnation processes on any of the plaques investigated. Of the three methods, the high temperature electrochemical impregnation process depends on the largest number of variables. If they are properly determined and regulated, this process may allow the closest control over the deposition of active material. Also, weakening of the plaque structure due to conversion is considerably less than with the conventional impregnation methods. Of great practical importance is that plaques can be impregnated in a one-step process.

The performance of negative plates appears to be much more dependent on manufacturing variables. Negative plates prepared by the high temperature electrochemical impregnation process show a significantly more favorable capacity retention than those prepared by either of the two conversion processes. This reflects probably a more uniform distribution of active material throughout the plaque structure. Plaque structure also is of importance. Slurry-coated plaques result in negatives with less capacity change. It is believed that the responsible parameter is the lower porosity of these plaques compared to the loose sinters rather than specific structural differences. A lower loading level is also more favorable for the capacity retention of negative plates.

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APPENDIX A

YATES' PROCEDURE FOR FACTORIAL EVALUATION

A. Estimation of Main Effects and Interactions

Yates' method is a systematic method for obtaining estimates of main effects and interactions for two-level factorials. The first step in the Yates' procedure is to make a table with n + 2 columns, where n is the number of factors in the factorial experiment. The treatment combinations are listed in standardized order in the first column, and after following the prescribed procedure, estimated main effects and interactions result in the last column (column n + 2). The order in which the treatment combinations are listed in column 1 determines the order of estimated effects in column n + 2.

The standard order for four factors in (Table A-1): (1), a, b, ab, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, abcd.

Table A-1. Factorial Terms for Four-Factor Experiment

		A_0		A_1	
		B_0	B_1	B_0	B_1
C_0	D_0	(1)	b	a	ab
	D_1	d	bd	ad	abd
C_1	D_0	c	bc	ac	abc
	D_1	cd	bcd	acd	abcd

The estimated main effects and interactions for four factors also appear in a standard order: T, A, B, AB, C, AC, BC, ABC, D, AD, BD, ABD, CD, ACD, BCD, ABCD, etc.

The systematic procedure for Yates' method is as follows:

1. Make a table with n + 2 columns (see Table A-2). In the first column, list the treatment combinations in standard order.

2. In column 2, enter the observed yield or response corresponding to each treatment combination listed in column 1.

3. In the top half of column 3, enter, in order, the sums of consecutive pairs of entries in column 2. In the bottom half of the column enter, in order, the differences between the same consecutive pairs of entries, i.e., second entry minus first entry, fourth entry minus third entry, etc.

4. Obtain columns 4, 5, . . . , n + 2, in the same manner as column 3, i.e., by obtaining in each case the sums and differences of the pairs in the preceding column in the manner described in step 3.

5. The entries in the last column (column n + 2) are called gT, gA, gB, gAB, etc., corresponding to the ordered effects T, A, B, AB, etc. Estimates of main effects and interactions are obtained by dividing the appropriate g by $2n^{-1}$. gT divided by $2n^{-1}$ is the overall mean.

NOTE: The reamining steps of this procedure are checks on the computation.

6. The sum of all the 2n individual responses (column 2) should equal the total given in the first entry of the last column (column n + 2).

7. The sum of the squares of the individual responses (column 2) should equal the sum of the squares in the entries of the last column (column n + 2) divided by 2n.

8. For any main effect, the entry in the last column (column n + 2) equals the sum of the responses in which that factor is at its lower level.

An example of a four-factor experiment analyzed by the Yates' method is given in Table A-2.

B. Procedure for Testing for Significance of Main Effects and Interactions

1. Choose α, the level of significance.

2. If there is no available estimate of the variation due to experimental error, find the sum of squares of the g's corresponding to interactions of three or more factors in Table A-2.

3. To obtain s^2, divide the sum of squares obtained in step 2 by $2^n\nu$, where ν is the number of interactions included. In a 2^n factorial, the number of third and higher interactions will be $2^n-(n^2+n+2)/2$. If an independent estimate of the variation due to experimental error is available, use this s^2.

4. Look up $t_1 = \alpha/2$ for ν degrees of freedom. If higher order interactions are used to obtain s^2, ν is the number of interactions included. If an independent estimate of s^2 is used, ν is the degree of freedom associated with this estimate.

5. Compute:

$$w = (2^n)^{\frac{1}{2}} t_{1-\alpha/2} S.$$

6. For any main effect of interaction X, if the absolute value of gx is greater than w, conclude that X is different from zero; e.g., if $|gA| > w$, conclude that the A effect is different from zero. Otherwise, there is no reason to believe that X is different from zero.

For the above example, the value of w is $|2.61|$, so that we may conclude that since $|gA| = 12.9$ and $|gAB| = 3.5$, the effect of factor A is significant and there is an interaction between factors A and B.

The analysis presented above assumes that apart from the factors varied, all other conditions were uniform throughout the experiment.

Table A-2. Example of Yates' Analysis of Four-Factor Experiment

1 Treatment Combination	2 Response (Yield)	3	4	5	6 g
(1)	4.2	7.3	14.7	29.2	57.5 = gT
a	3.1	7.4	14.5	28.3	-12.9 = gA
b	4.5	6.7	14.5	-5.2	2.5 = gB
ab	2.9	7.8	13.8	-7.7	-3.5 = gAB
c	3.9	7.0	-2.7	1.2	-0.9 = gC
ac	2.8	7.5	-2.5	1.3	-0.5 = gAC
bc	4.6	6.5	-3.5	-0.8	1.3 = gBC
abc	3.2	7.3	-4.2	-2.7	0.5 = gABC
d	4.0	-1.1	-0.1	-0.2	-0.9 = gD
ad	3.0	-1.6	1.1	-0.7	-2.5 = gAD
bd	5.0	-1.1	0.5	0.2	0.1 = gBD
abd	2.5	-1.4	0.8	-0.7	-1.9 = gABD
cd	4.0	-1.0	-0.5	1.0	-0.5 = gCD
acd	2.5	-2.5	-0.3	0.3	-0.9 = gACD
bcd	5.0	-1.5	-1.5	0.2	-0.7 = gBCD
abcd	2.3	-2.7	-1.2	0.3	0.1 = gABCD
Total	57.5				
Sum of Squares	219.15				3506.40

APPENDIX B

Effect of manufacturing variables on delivered capacity of Positive and Negative plates; computer printout of factorial analysis. (Value z reflects 95% comfidence limit; for 80% confidence limit, multiply by 0.575.)

```
NI-CD FACTORIAL      CTH - CEND
    COMB =
'+C0,C1/A1,A2'

TREATMENT RESPONSE             G                G/8             INT
T                  89.0       1424.5           178.1       T
A                 106.0         41.5             5.2       A
B                  84.0        -31.5            -3.9       B
AB                 86.0          5.5             0.7       AB
C                  97.5        -16.5            -2.1       C
AC                 89.0          2.5             0.3       AC
BC                 84.5         19.5             2.4       BC
ABC               116.0         34.5             4.3       ABC
D                  89.0        -79.5            -9.9       D
AD                 89.0        -42.5            -5.3       AD
BD                 88.5         -9.5            -1.2       BD
ABD                89.0        -44.5            -5.6       ABD
CD                 79.5        -60.5            -7.6       CD
ACD                89.0         -5.5            -0.7       ACD
BCD                79.5        -58.5            -7.3       BCD
ABCD               69.0        -75.5            -9.4       ABCD
       S =          1424.5000
LEVEL OF SIGNIFICANCE
       Z =           127.63792
```

```
NI-CD FACTORIAL      CTH - CEND
    COMB = '+ C0,C1/A0,A2'

TREATMENT RESPONSE             G                G/8             INT
T                  90.5       1414.5           176.8       T
A                 106.0         29.5             3.7       A
B                 108.0         39.5             4.9       B
AB                 86.5         -9.5            -1.2       AB
C                  78.0        -49.5            -6.2       C
AC                 84.0          9.5             1.2       AC
BC                 89.0         13.5             1.7       BC
ABC               116.0         32.5             4.1       ABC
D                  81.5       -101.5           -12.7       D
AD                 81.5        -24.5            -3.1       AD
BD                 81.0        -42.5            -5.3       BD
ABD                97.0         22.5             2.8       ABD
CD                 84.0         -1.5            -0.2       CD
ACD                82.0        -68.5            -8.6       ACD
BCD                80.5        -76.5            -9.6       BCD
ABCD               69.0        -83.5           -10.4       ABCD
       S =         1414.5000
LEVEL OF SIGNIFICANCE
       Z =          158.81727
>
```

```
NI-CD FACTORIAL      CTH - CEND
    COMB = '+ C0,C1/A0,A1'

TREATMENT RESPONSE          G              G/8          INT
T               90.5      1385.0          173.1      T
A               97.5         0.0            0.0      A
B              108.0         5.0            0.6      B
AB              84.0       -44.0           -5.5      AB
C               78.0       -40.0           -5.0      C
AC              97.5        19.0            2.4      AC
BC              89.0       -16.0           -2.0      BC
ABC             84.5         3.0            0.4      ABC
D               81.5       -73.0           -9.1      D
AD              81.5         4.0            0.5      AD
BD              81.0         1.0            0.1      BD
ABD             88.5        66.0            8.2      ABD
CD              84.0        22.0            2.7      CD
ACD             79.5       -45.0           -5.6      ACD
BCD             80.5        -4.0           -0.5      BCD
ABCD            79.5       -11.0           -1.4      ABCD
       S =      1385
LEVEL OF SIGNIFICANCE
       Z =          92.891052
>
```

```
NI-CD FACTORIAL      CTH - CEND
    COMB = '+ C0,XAC2/A0,A1'

TREATMENT RESPONSE          G              G/8          INT
T               90.5      1326.5          165.8      T
A               97.5        -6.5           -0.8      A
B              108.0       -18.5           -2.3      B
AB              84.0       -23.5           -2.9      AB
C               70.5       -98.5          -12.3      C
AC              86.0        12.5            1.6      AC
BC              84.0       -39.5           -4.9      BC
ABC             76.5        23.5            2.9      ABC
D               81.5       -67.5           -8.4      D
AD              81.5        11.5            1.4      AD
BD              81.0       -34.5           -4.3      BD
ABD             88.5        84.5           10.6      ABD
CD              89.5        27.5            3.4      CD
ACD             75.5       -37.5           -4.7      ACD
BCD             61.5       -39.5           -4.9      BCD
ABCD            70.5         7.5            0.9      ABCD
       S =      1326.5000
LEVEL OF SIGNIFICANCE
       Z =      119.01953
>
```

```
NI-CD FACTORIAL      CTH - CEND
    COMB = '+ C0C2/A1,A2'

TREATMENT RESPONSE              G                G/8           INT
T               97.5         1357.5            169.7      T
A              106.0           37.5              4.7      A
B               84.0           -2.5             -0.3      B
AB              86.0           39.5              4.9      AB
C               86.0          -86.5            -10.8      C
AC              79.0           -0.5             -0.1      AC
BC              76.5           19.5              2.4      BC
ABC             87.5           35.5              4.4      ABC
D               81.5          -47.5             -5.9      D
AD              81.5            8.5              1.1      AD
BD              88.5           66.5              8.3      BD
ABD             97.0           16.5              2.1      ABD
CD              75.5            2.5              0.3      CD
ACD             73.0           12.5              1.6      ACD
BCD             70.5          -45.5             -5.7      BCD
ABCD            87.5          -13.5             -1.7      ABCD
       S =        1357.5000
LEVEL OF SIGNIFICANCE
       Z =          72.182857
`
```

```
NI-CD FACTORIAL      CTH - CEND
    COMB = '+C0,C2/A0,A2'

TREATMENT RESPONSE              G                G/8           INT
T               90.5         1364.0            170.5      T
A              106.0           31.0              3.9      A
B              108.0           21.0              2.6      B
AB              86.0           16.0              2.0      AB
C               70.5          -99.0            -12.4      C
AC              79.0           12.0              1.5      AC
BC              84.0           -4.0             -0.5      BC
ABC             87.5           59.0              7.4      ABC
D               81.5          -59.0             -7.4      D
AD              81.5           20.0              2.5      AD
BD              81.0          -18.0             -2.2      BD
ABD             97.0          101.0             12.6      ABD
CD              89.5           40.0              5.0      CD
ACD             73.0          -25.0             -3.1      ACD
BCD             61.5          -53.0             -6.6      BCD
ABCD            87.5           -6.0             -0.8      ABCD
       S =      1364
LEVEL OF SIGNIFICANCE
       Z =         150.58248
>
```

```
NI-CD FACTORIAL     CTH - CEND
    COMB = '+ C1,C2/A0,A2'

TREATMENT RESPONSE            G                G/8            INT
T               78.0       1316.0            164.5       T
A               84.0         40.0              5.0       A
B               89.0         36.0              4.5       B
AB             116.0         48.0              6.0       AB
C               70.5        -49.0             -6.1       C
AC              79.0          1.0              0.1       AC
BC              85.0        -17.0             -2.1       BC
ABC             87.5         25.0              3.1       ABC
D               84.0        -62.0             -7.7       D
AD              82.0        -48.0             -6.0       AD
BD              80.5        -96.0            -12.0       BD
ABD             69.0         18.0              2.2       ABD
CD              89.5         41.0              5.1       CD
ACD             73.0         45.0              5.6       ACD
BCD             61.5         23.0              2.9       BCD
ABCD            87.5         79.0              9.9       ABCD
       S =        1316
LEVEL OF SIGNIFICANCE
       Z =          113.49735
>
```

```
NI-CD FACTORIAL     CTH - CEND
    COMB = '+ C1,C2/A1,A2,'

TREATMENT RESPONSE            G                G/8            INT
T               97.5       1327.5            165.9       T
A               83.0         28.5              3.6       A
B               84.5         14.5              1.8       B
AB             116.0         69.5              8.7       AB
C               86.0        -56.5             -7.1       C
AC              79.0          8.5              1.1       AC
BC              76.5          2.5              0.3       BC
ABC             87.5          5.5              0.7       ABC
D               79.5        -92.5            -11.6       D
AD              83.0        -13.5             -1.7       AD
BD              79.5        -23.5             -2.9       BD
ABD             69.0        -58.5             -7.3       ABD
CD              75.5         47.5              5.9       CD
ACD             73.0         34.5              4.3       ACD
BCD             70.5         44.5              5.6       BCD
ABCD            87.5         61.5              7.7       ABCD
       S =        1327.5000
LEVEL OF SIGNIFICANCE
       Z =          117.28523
>
```

```
NI-CD FACTORIAL      CTH - CEND
    COMB = '+ C1,C2/A0,A1'

TREATMENT RESPONSE           G               G/8          INT
T               78.0      1287.5           160.9      T
A               97.5        11.5             1.4      A
B               89.0       -33.5            -4.2      B
AB              84.5       -21.5            -2.7      AB
C               70.5       -57.5            -7.2      C
AC              86.0        -7.5            -0.9      AC
BC              85.0       -22.5            -2.8      BC
ABC             76.5        19.5             2.4      ABC
D               84.0       -46.5            -5.8      D
AD              79.5       -32.5            -4.1      AD
BD              80.5       -39.5            -4.9      BD
ABD             79.5        74.5             9.3      ABD
CD              89.5         4.5             0.6      CD
ACD             75.5         8.5             1.1      ACD
BCD             61.5       -36.5            -4.6      BCD
ABCD            70.5        19.5             2.4      ABCD
       S =       1287.5000
LEVEL OF SIGNIFICANCE
       Z =         100.99319
>
```

```
NI-CD FACTORIAL     C RETAINED OVER 100 CYCLES
    COMB = 'C0,C1/A1,A2 +'

TREATMENT RESPONSE              G              G/8            INT
T               9[illegible].0          1584.5          198.1     T
A             108.0            35.5            4.4     A
B              82.5           -36.5           -4.6     B
AB            102.0            36.5            4.6     AB
C             106.0            19.5            2.4     C
AC              9[illegible].0         -15.5           -1.9     AC
BC             89.5            18.5            2.3     BC
ABC           114.5            21.5            2.7     ABC
D               9[illegible].0         -16.5           -2.1     D
AD              9[illegible].0         -57.5           -7.2     AD
BD             98.0            10.5            1.3     BD
ABD            95.0           -48.5           -6.1     ABD
CD             10[illegible].5         -15.5           -1.9     CD
ACD             9[illegible].0           5.5            0.7     ACD
BCD             9[illegible].0         -24.5           -3.1     BCD
ABCD           93.5           -21.5           -2.7     ABCD
        S =       1584.50
LEVEL OF SIGNIFICANCE
        Z =            71.870832
>
```

```
NI-CD FACTORIAL     C RETAINED OVER 100 CYCLES
    COMB = '+C0,C1/A0,A2'

TREATMENT RESPONSE              G              G/8            INT
T              90.0          1574.0          196.7     T
A             108.0            26.0            3.2     A
B              99.0            30.0            3.7     B
AB            102.0           -26.0           -3.2     AB
C              95.0            23.0            2.9     C
AC            100.0             1.0            0.1     AC
BC             97.0            15.0            1.9     BC
ABC           114.5            21.0            2.6     ABC
D              93.0           -37.0           -4.6     D
AD             93.0           -61.0           -7.6     AD
BD             99.5            -9.0           -1.1     BD
ABD            91.0           -21.0           -2.6     ABD
CD             95.0             8.0            1.0     CD
ACD            98.0            -2.0           -0.3     ACD
BCD           105.5           -12.0           -1.5     BCD
ABCD           93.5           -34.0           -4.2     ABCD
        S =      1574
LEVEL OF SIGNIFICANCE
        Z =           53.757882
>
```

```
NI-CD FACTORIAL    C RETAINED OVER 100 CYCLES
    COMB = '+ C0,C1/A0,A1'

TREATMENT RESPONSE            G              G/8          INT
T               90.0      1538.5            192.3      T
A               95.0        -9.5             -1.2      A
B               99.0         1.5              0.2      B
AB              82.5       -54.5             -6.8      AB
C               95.0        38.5              4.8      C
AC             106.0        16.5              2.1      AC
BC              97.0       -14.5             -1.8      BC
ABC             89.5        -8.5             -1.1      ABC
D               93.0        30.5              3.8      D
AD              93.0         6.5              0.8      AD
BD              99.5        37.5              4.7      BD
ABD             98.0        25.5              3.2      ABD
CD              95.0        -3.5             -0.4      CD
ACD            101.5       -13.5             -1.7      ACD
BCD            105.5         7.5              0.9      BCD
ABCD            99.0       -14.5             -1.8      ABCD
       S =      1538.5000
LEVEL OF SIGNIFICANCE
       Z =          39.349741
>
```

```
C RETAINED OVER 100 CYCLES
    COMB = 'C0,C2/A0,A1'

TREATMENT RESPONSE            G              G/8          INT
T               90.0      1472.0            184.0      T
A               91.0       -37.0             -4.6      A
B               99.0        -4.0             -0.5      B
AB              82.5       -61.0             -7.6      AB
C               87.5       -16.0             -2.0      C
AC              99.5         1.0              0.1      AC
BC              92.0       -32.0             -4.0      BC
ABC             76.5       -27.0             -3.4      ABC
D               93.0        36.0              4.5      D
AD              91.0         1.0              0.1      AD
BD              99.5        32.0              4.0      BD
ABD             98.0        29.0              3.6      ABD
CD              92.5        -2.0             -0.3      CD
ACD             93.5       -23.0             -2.9      ACD
BCD            101.0         6.0              0.8      BCD
ABCD            85.5        -7.0             -0.9      ABCD
       S =      1472
LEVEL OF SIGNIFICANCE
       Z =          53.733285
>
```

```
C RETAINED OVER 100 CYCLES
    COMB = 'C0,C2/A0,A2'

TREATMENT RESPONSE            G              G/8          INT
T                 90.0      1492.5          186.6      T
A                108.0       -16.5           -2.1      A
B                 99.0        18.5            2.3      B
AB               102.0       -38.5           -4.8      AB
C                 87.5       -54.5           -6.8      C
AC                85.5       -37.5           -4.7      AC
BC                92.0        -0.5           -0.1      BC
ABC               83.5         4.5            0.6      ABC
D                 93.0        -2.5           -0.3      D
AD                91.0       -37.5           -4.7      AD
BD                99.5         7.5            0.9      BD
ABD               91.0         4.5            0.6      ABD
CD                92.5        46.5            5.8      CD
ACD               89.5        25.5            3.2      ACD
BCD              101.0         0.5            0.1      BCD
ABCD              87.5       -12.5           -1.6      ABCD
       S =         1492.5000
LEVEL OF SIGNIFICANCE
       Z =           33.467468
>
```

```
C RETAINED OVER 100 CYCLES
    COMB = 'C0,C2/A1,A2'

TREATMENT RESPONSE            G              G/8          INT
T                 91.0      1455.5          181.9      T
A                108.0        20.5            2.6      A
B                 82.5       -42.5           -5.3      B
AB               102.0        22.5            2.8      AB
C                 99.5       -53.5           -6.7      C
AC                85.5       -38.5           -4.8      AC
BC                76.5       -27.5           -3.4      BC
ABC               83.5        31.5            3.9      ABC
D                 91.0        -1.5           -0.2      D
AD                91.0       -38.5           -4.8      AD
BD                98.0        36.5            4.6      BD
ABD               91.0       -24.5           -3.1      ABD
CD                93.5        23.5            2.9      CD
ACD               89.5        48.5            6.1      ACD
BCD               85.5        -6.5           -0.8      BCD
ABCD              87.5        -5.5           -0.7      ABCD
       S =        1455.5000
LEVEL OF SIGNIFICANCE
       Z =          72.875493
>
```

```
NI-CD FACTORIAL     C RETAINED OVER 10  CYCLES
    COMB = '+C1,C2/A1,A2'

TREATMENT RESPONSE          G              G/8          INT
T              106.0     1461.5          182.7       T
A               91.0        6.5            0.8       A
B               89.5       -6.5           -0.8       B
AB             114.5       46.5            5.8       AB
C               85.5     -110.5          -13.8       C
AC              85.5       18.5            2.3       AC
BC              76.5      -20.5           -2.6       BC
ABC             83.5      -43.5           -5.4       ABC
D              101.5       -2.5           -0.3       D
AD              91.0      -27.5           -3.4       AD
BD              9 .0        1.5            0.2       BD
ABD             93.5      -47.5           -5.9       ABD
CD              84.0       29.5            3.7       CD
ACD             89.5       24.5            3.1       ACD
BCD             85.5       15.5            1.9       BCD
ABCD            85.5       22.5            2.8       ABCD
       S =        1461.50
LEVEL OF SIGNIFICANCE
       Z =           85.23 594
>
```

```
C RETAINED OVER 100 CYCLES
    COMB = 'C1,C2/A0,A2'

TREATMENT RESPONSE          G              G/8          INT
T               95.0     1501.5          187.7       T
A               91.0      -29.5           -3.7       A
B               97.0       47.5            5.9       B
AB             114.5       -3.5           -0.4       AB
C               87.5      -63.5           -7.9       C
AC              85.5      -24.5           -3.1       AC
BC              92.0      -29.5           -3.7       BC
ABC             83.5      -30.5           -3.8       ABC
D               95.0        9.5            1.2       D
AD              91.0      -35.5           -4.4       AD
BD             105.5       -8.5           -1.1       BD
ABD             93.5      -33.5           -4.2       ABD
CD              92.5       34.5            4.3       CD
ACD             89.5       23.5            2.9       ACD
BCD            101.0       16.5            2.1       BCD
ABCD            87.5       25.5            3.2       ABCD
       S =        1501.5000
LEVEL OF SIGNIFICANCE
       Z =           68.286554
>
```

```
C RETAINED OVER 100 CYCLES
    COMB = 'C1.C2/A0,A1'

TREATMENT RESPONSE           G              G/8          INT
T               95.0      1516.5           189.6       T
A              106.0       -14.5            -1.8       A
B               97.0       -24.5            -3.1       B
AB              89.5       -75.5            -9.4       AB
C               87.5       -60.5            -7.6       C
AC              99.5       -21.5            -2.7       AC
BC              92.0       -11.5            -1.4       BC
ABC             76.5       -12.5            -1.6       ABC
D               95.0        30.5             3.8       D
AD             101.5       -14.5            -1.8       AD
BD             105.5        41.5             5.2       BD
ABD             99.0        16.5             2.1       ABD
CD              92.5         3.5             0.4       CD
ACD             93.5        -7.5            -0.9       ACD
BCD            101.0        -3.5            -0.4       BCD
ABCD            85.5         5.5             0.7       ABCD
       S =       1516.5000
LEVEL OF SIGNIFICANCE
       Z =         26.401303
>
```

```
NI-CD FACTORIAL      CTH - CEND
    COMB = '- C0,C1/A1A2'

TREATMENT RESPONSE              G                  G/8           INT
T                  60.0        962.5              120.3       T
A                  94.0         65.0                8.2       A
B                  56.5        -41.5               -5.2       B
AB                 62.0        -26.5               -3.3       AB
C                  52.5        -62.5               -7.8       C
AC                 60.0        -25.5               -3.2       AC
BC                 51.5         29.5                3.7       BC
ABC                63.0         18.5                2.3       ABC
D                  60.0        -36.5               -4.6       D
AD                 60.0        -51.5               -6.4       AD
BD                 57.0         25.5                3.2       BD
ABD                63.0         22.5                2.8       ABD
CD                 5[illegible].0         28.5                3.6       CD
ACD                60.0         15.5                1.9       ACD
BCD                5[illegible].5        -45.5               -5.7       BCD
ABCD               52.0        -46.5               -5.8       ABCD
       S =            962.50
LEVEL OF SIGNIFICANCE
       Z =              83.873[illegible]4
>
```

```
NI-CD FACTORIAL      CTH - CEND
    COMB = '- C0,C1/A0,A2'

TREATMENT RESPONSE              G                  G/8           INT
T                  64.5        971.0              121.4       T
A                  90.0         76.0                9.5       A
B                  59.5        -29.0               -3.6       B
AB                 62.0        -44.0               -5.5       AB
C                  45.5        -73.0               -9.1       C
AC                 65.0        -32.0               -4.0       AC
BC                 57.5         45.0                5.6       BC
ABC                66.0         10.0                1.2       ABC
D                  55.0        -49.0               -6.1       D
AD                 70.0        -36.0               -4.5       AD
BD                 55.0         11.0                1.4       BD
ABD                66.0         24.0                3.0       ABD
CD                 55.0         11.0                1.4       CD
ACD                55.0        -32.0               -4.0       ACD
BCD                55.5        -47.0               -5.9       BCD
ABCD               49.5        -14.0               -1.7       ABCD
       S =         971
LEVEL OF SIGNIFICANCE
       Z =              73.667114
>
```

```
NI-CD FACTORIAL        CTH - CEND
    COMB = '-C0,C1/A0,A1'

TREATMENT RESPONSE            G               G/8           INT
T                 64.5        911.5           113.9       T
A                 75.0         16.5             2.1       A
B                 59.5        -24.5            -3.1       B
AB                56.5        -39.5            -4.9       AB
C                 45.5        -63.5            -7.9       C
AC                52.5        -22.5            -2.8       AC
BC                57.5         38.5             4.8       BC
ABC               51.5          3.5             0.4       ABC
D                 55.0        -13.5            -1.7       D
AD                65.0         -0.5            -0.1       AD
BD                55.0          0.5             0.1       BD
ABD               57.0         13.5             1.7       ABD
CD                55.0         33.5             4.2       CD
ACD               55.5         -9.5            -1.2       ACD
BCD               55.5        -30.5            -3.8       BCD
ABCD              51.0          2.5             0.3       ABCD
          S =        911.50000
LEVEL OF SIGNIFICANCE
          Z =         40.180872
>
```

```
NI-CD FACTORIAL        CTH - CEND
    COMB = '-C0,C2/A0,A1'

TREATMENT RESPONSE            G               G/8           INT
T                 64.5        986.5           123.3       T
A                 75.0         58.5             7.3       A
B                 59.5        -68.5            -8.6       B
AB                56.5         -6.5            -0.8       AB
C                 62.5         11.5             1.4       C
AC                76.0         19.5             2.4       AC
BC                58.0         -5.5            -0.7       BC
ABC               67.5         36.5             4.6       ABC
D                 55.0        -52.5            -6.6       D
AD                65.0         -2.5            -0.3       AD
BD                55.0          4.5             0.6       BD
ABD               57.0         28.5             3.6       ABD
CD                65.5         -5.5            -0.7       CD
ACD               64.0        -11.5            -1.4       ACD
BCD               44.0        -26.5            -3.3       BCD
ABCD              61.5         17.5             2.2       ABCD
          S =        986.50000
LEVEL OF SIGNIFICANCE
          Z =         65.902408
>
```

```
NI-CD FACTORIAL      CTH - CEND
       COMB = '- C0,C2/A0,A2'

TREATMENT RESPONSE             G               G/8           INT
T                   64.5       999.0          124.9     T
A                   90.0        71.0            8.9     A
B                   59.5       -46.0           -5.7     B
AB                  62.0        16.0            2.0     AB
C                   62.5       -45.0           -5.6     C
AC                  68.0       -37.0           -4.6     AC
BC                  58.0        28.0            3.5     BC
ABC                 73.5        70.0            8.7     ABC
D                   55.0       -77.0           -9.6     D
AD                  70.0       -27.0           -3.4     AD
BD                  55.0        18.0            2.2     BD
ABD                 66.0        42.0            5.2     ABD
CD                  65.5       -17.0           -2.1     CD
ACD                 47.0       -23.0           -2.9     ACD
BCD                 44.0       -40.0           -5.0     BCD
ABCD                58.5         4.0            0.5     ABCD
            S =        999
LEVEL OF SIGNIFICANCE
            Z =        107.91464
>
```

```
NI-CD FACTORIAL      CTH - CEND
       COMB = '-C0,C2/A1,A2'

TREATMENT RESPONSE             G               G/8           INT
T                   75.0      1057.5          132.2     T
A                   90.0        12.5            1.6     A
B                   56.5       -52.5           -6.6     B
AB                  62.0        22.5            2.8     AB
C                   76.0       -25.5           -3.2     C
AC                  68.0       -56.5           -7.1     AC
BC                  67.5        64.5            8.1     BC
ABC                 73.5        33.5            4.2     ABC
D                   65.0       -79.5           -9.9     D
AD                  70.0       -24.5           -3.1     AD
BD                  57.0        46.5            5.8     BD
ABD                 66.0        13.5            1.7     ABD
CD                  64.0       -28.5           -3.6     CD
ACD                 47.0       -11.5           -1.4     ACD
BCD                 61.5       -22.5           -2.8     BCD
ABCD                58.5       -13.5           -1.7     ABCD
            S =      1057.5000
LEVEL OF SIGNIFICANCE
            Z =         53.005641
>
```

```
NI-CD FACTORIAL     CTH - CEND
    COMB = '- C1,C2/A1A2'

TREATMENT RESPONSE              G                  G/8          INT
T               52.5          966.0              120.7       T
A               60.0           -2.0               -0.3       A
B               51.5            0.0                0.0       B
AB              63.0           24.0                3.0       AB
C               76.0           66.0                8.2       C
AC              68.0          -42.0               -5.2       AC
BC              67.5           12.0                1.5       BC
ABC             73.5           32.0                4.0       ABC
D               57.5          -58.0               -7.2       D
AD              60.0          -36.0               -4.5       AD
BD              53.5            2.0                0.3       BD
ABD             52.0          -12.0               -1.5       ABD
CD              64.0          -50.0               -6.2       CD
ACD             47.0            0.0                0.0       ACD
BCD             61.5           22.0                2.7       BCD
ABCD            58.5           12.0                1.5       ABCD
      S =          966
LEVEL OF SIGNIFICANCE
      Z =             48.727064
>
```

```
NI-CD FACTORIAL     CTH - CEND
    COMB = '-C1,C2/A0,A2'

TREATMENT RESPONSE              G                  G/8          INT
T               45.5          926.0              115.7       T
A               65.0           39.0                4.9       A
B               57.5           -1.0               -0.1       B
AB              66.0           26.0                3.2       AB
C               62.5           28.0                3.5       C
AC              68.0           -5.0               -0.6       AC
BC              58.0          -17.0               -2.1       BC
ABC             73.5           60.0                7.5       ABC
D               55.0          -66.0               -8.2       D
AD              55.0          -59.0               -7.4       AD
BD              55.5          -29.0               -3.6       BD
ABD             49.5           28.0                3.5       ABD
CD              65.5          -28.0               -3.5       CD
ACD             47.0            9.0                1.1       ACD
BCD             44.0            7.0                0.9       BCD
ABCD            58.5           18.0                2.2       ABCD
      S =          926
LEVEL OF SIGNIFICANCE
      Z =             79.974219
>
```

```
 NI-CD FACTORIAL      CTH - CEND
     COMB = '-C1,C2/A0,A1'

 TREATMENT RESPONSE              G                   G/8             INT
 T                   45.5        923.0               115.4        T
 A                   52.5         36.0                 4.5        A
 B                   57.5        -30.0                -3.7        B
 AB                  51.5         -3.0                -0.4        AB
 C                   62.5         75.0                 9.4        C
 AC                  76.0         42.0                 5.2        AC
 BC                  58.0        -44.0                -5.5        BC
 ABC                 67.5         33.0                 4.1        ABC
 D                   55.0        -19.0                -2.4        D
 AD                  55.5        -12.0                -1.5        AD
 BD                  55.5        -26.0                -3.2        BD
 ABD                 51.0         31.0                 3.9        ABD
 CD                  65.5        -39.0                -4.9        CD
 ACD                 64.0         -2.0                -0.3        ACD
 BCD                 44.0          4.0                 0.5        BCD
 ABCD                61.5         15.0                 1.9        ABCD
         S =           923
 LEVEL OF SIGNIFICANCE
         Z =             55.081837
 >
```

```
    COMB = '- C0,C1/A1,A2'

TREATMENT RESPONSE             G                G/8          INT
T               84.0        1343.0            167.9       T
A               99.5          47.0              5.9       A
B               83.5          -7.0             -0.9       B
AB              85.0          -9.0             -1.1       AB
C               77.5         -29.0             -3.6       C
AC              84.0           9.0              1.1       AC
BC              84.0          27.0              3.4       BC
ABC             87.5          15.0              1.9       ABC
D               84.0         -27.0             -3.4       D
AD              84.0          -7.0             -0.9       AD
BD              82.0           3.0              0.4       BD
ABD             84.0          25.0              3.1       ABD
CD              78.0           9.0              1.1       CD
ACD             84.0          23.0              2.9       ACD
BCD             75.0         -23.0             -2.9       BCD
ABCD            87.0          -7.0             -0.9       ABCD
      S =         1343
LEVEL OF SIGNIFICANCE
      Z =           50.864232
>
```

```
NI-CD FACTORIAL    C RETAINED OVER 100 CYCLES
    COMB = '- C0,C1/A0,A2'

TREATMENT RESPONSE             G                G/8          INT
T               79.5        1338.0            167.2       T
A               99.5          91.0             11.4       A
B               76.5         -11.0             -1.4       B
AB              85.0         -18.0             -2.2       AB
C               78.0          25.0              3.1       C
AC              91.0          -6.0             -0.8       AC
BC              83.0          24.0              3.0       BC
ABC             91.0           5.0              0.6       ABC
D               74.0         -29.0             -3.6       D
AD              84.0          -8.0             -1.0       AD
BD              74.0          14.0              1.7       BD
ABD             84.0          15.0              1.9       ABD
CD              78.5          20.0              2.5       CD
ACD             90.0           9.0              1.1       ACD
BCD             80.0         -21.0             -2.6       BCD
ABCD            90.0          -8.0             -1.0       ABCD
      S =        1338
LEVEL OF SIGNIFICANCE
      Z =           33.244531
>
```

```
NI-CD FACTORIAL     C RETAINED OVER 100 CYCLES
    COMB = '- C0,C1/A0,A1'

TREATMENT RESPONSE              G               G/8           INT
T                   79.5     1259.5            157.4     T
A                   83.0       12.5              1.6     A
B                   76.5       -1.5             -0.2     B
AB                  83.5       -8.5             -1.1     AB
C                   78.0       -9.5             -1.2     C
AC                  77.5      -40.5             -5.1     AC
BC                  83.0        3.5              0.4     BC
ABC                 84.0      -15.5             -1.9     ABC
D                   74.0      -30.5             -3.8     D
AD                  82.0       -9.5             -1.2     AD
BD                  74.0      -19.5             -2.4     BD
ABD                 82.0      -18.5             -2.3     ABD
CD                  78.5       -9.5             -1.2     CD
ACD                 78.0      -20.5             -2.6     ACD
BCD                 80.0      -24.5             -3.1     BCD
ABCD                66.0      -11.5             -1.4     ABCD
       S =        1259.5000
LEVEL OF SIGNIFICANCE
       Z =          47.895874
>
```

```
NI-CD FACTORIAL     C RETAINED OVER 100 CYCLES
    COMB = '- C0,C2/A0,A1'

TREATMENT RESPONSE              G               G/8           INT
T                   79.5     1341.5            167.7     T
A                   83.0       28.5              3.6     A
B                   76.5      -27.5             -3.4     B
AB                  83.5        9.5              1.2     AB
C                   91.0       72.5              9.1     C
AC                  92.0      -24.5             -3.1     AC
BC                  89.0      -22.5             -2.8     BC
ABC                 89.5        2.5              0.3     ABC
D                   74.0      -26.5             -3.3     D
AD                  82.0        4.5              0.6     AD
BD                  74.0      -13.5             -1.7     BD
ABD                 82.0        3.5              0.4     ABD
CD                  93.0       -5.5             -0.7     CD
ACD                 90.0       -6.5             -0.8     ACD
BCD                 79.5      -18.5             -2.3     BCD
ABCD                83.0       10.5              1.3     ABCD
       S =        1341.5000
LEVEL OF SIGNIFICANCE
       Z =          26.048430
>
```

```
NI-CD FACTORIAL     C RETAINED OVER 100 CYCLES
     COMB = '-C0,C2/A0,A2'

TREATMENT RESPONSE           G             G/8          INT
T                 79.5     1364.0        170.5     T
A                 99.5       51.0          6.4     A
B                 76.5      -16.0         -2.0     B
AB                85.0       21.0          2.6     AB
C                 91.0       51.0          6.4     C
AC                92.5      -46.0         -5.7     AC
BC                89.0       19.0          2.4     BC
ABC               93.5       44.0          5.5     ABC
D                 74.0      -49.0         -6.1     D
AD                84.0      -18.0         -2.2     AD
BD                74.0       21.0          2.6     BD
ABD               84.0       38.0          4.7     ABD
CD                93.0        0.0          0.0     CD
ACD               76.5       -1.0         -0.1     ACD
BCD               79.5      -14.0         -1.7     BCD
ABCD              92.5       15.0          1.9     ABCD
       S =        1364
LEVEL OF SIGNIFICANCE
       Z =          70.896228
>
```

```
NI-CD FACTORIAL     C RETAINED OVER 100 CYCLES
     COMB = '- C0,C2/A1,A2'

TREATMENT RESPONSE           G             G/8          INT
T                 83.0     1392.5        174.1     T
A                 99.5       22.5          2.8     A
B                 83.5       -6.5         -0.8     B
AB                85.0       11.5          1.4     AB
C                 92.0       26.5          3.3     C
AC                92.5      -21.5         -2.7     AC
BC                89.5       21.5          2.7     BC
ABC               93.5       41.5          5.2     ABC
D                 82.0      -44.5         -5.6     D
AD                84.0      -22.5         -2.8     AD
BD                82.0       24.5          3.1     BD
ABD               84.0       34.5          4.3     ABD
CD                90.0       -6.5         -0.8     CD
ACD               76.5        5.5          0.7     ACD
BCD               83.0       -3.5         -0.4     BCD
ABCD              92.5        4.5          0.6     ABCD
       S =        1392.5000
LEVEL OF SIGNIFICANCE
       Z =          62.716066
>
```

```
NI-CD FACTORIAL     C RETAINED OVER 100 CYCLES
      COMB = '- C1,C2/A1,A2'

TREATMENT  RESPONSE          G              G/8           INT
T               7 .5      1373.5          171.7       T
A              86.0         33.5            4.2       A
B              84.0         16.5            2.1       B
AB             8 .5         26.5            3.3       AB
C              92.0         45.5            5.7       C
AC             92.5        -32.5           -4.1       AC
BC             89.5         -1.5           -0.2       BC
ABC            93.5         26.5            3.3       ABC
D              78.0        -33.5           -4.2       D
AD             86.0         -1.5           -0.2       AD
BD             76.0          1.5            0.2       BD
ABD            8 .0         27.5            3.4       ABD
CD             90.0        -17.5           -2.2       CD
ACD            76.5        -15.5           -1.9       ACD
BCD            83.0         19.5            2.4       BCD
ABCD           92.5         11.5            1.4       ABCD
        S =       1373.500
LEVEL OF SIGNIFICANCE
        Z =          54.067464
>
```

```
NI-CD FACTORIAL     C RETAINED OVER 100 CYCLES
      COMB = '- C1,C2/A0,A2'

TREATMENT  RESPONSE          G              G/8           INT
T              78.0       1389.0          173.6       T
A              91.0         45.0            5.6       A
B              83.0          8.0            1.0       B
AB             91.0         26.0            3.2       AB
C              91.0         26.0            3.2       C
AC             92.5        -40.0           -5.0       AC
BC             89.0         -5.0           -0.6       BC
ABC            93.5         39.0            4.9       ABC
D              78.5        -29.0           -3.6       D
AD             90.0         -9.0           -1.1       AD
BD             80.0          0.0            0.0       BD
ABD            90.0         30.0            3.7       ABD
CD             93.0        -20.0           -2.5       CD
ACD            76.5        -10.0           -1.2       ACD
BCD            79.5          7.0            0.9       BCD
ABCD           92.5         23.0            2.9       ABCD
        S =     1389
LEVEL OF SIGNIFICANCE
        Z =          64.007058
>
```

```
NI-CD FACTORIAL    C RETAINED OVER 100 CYCLES
    COMB = '- C1,C2/A0,A1'

TREATMENT RESPONSE          G             G/8          INT
T              78.0        1332.0         166.5     T
A              77.5         -12.0          -1.5     A
B              83.0         -24.0          -3.0     B
AB             84.0          -6.0          -0.8     AB
C              91.0          82.0          10.2     C
AC             92.0          16.0           2.0     AC
BC             89.0         -26.0          -3.2     BC
ABC            89.5          18.0           2.2     ABC
D              78.5         -36.0          -4.5     D
AD             78.0         -16.0          -2.0     AD
BD             80.0         -38.0          -4.7     BD
ABD            66.0          -8.0          -1.0     ABD
CD             93.0           4.0           0.5     CD
ACD            90.0          14.0           1.7     ACD
BCD            79.5           6.0           0.8     BCD
ABCD           83.0          22.0           2.7     ABCD
       S =      1332
LEVEL OF SIGNIFICANCE
       Z =        38.203364
>
```