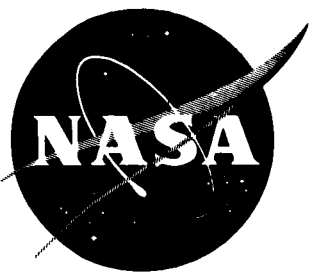


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**DEVELOPMENT OF LARGE-INTERNAL-SURFACE-AREA
NICKEL-METAL PLAQUES**

Third Quarterly Progress Report

(Period Covered: December 19, 1964, through March 18, 1965)

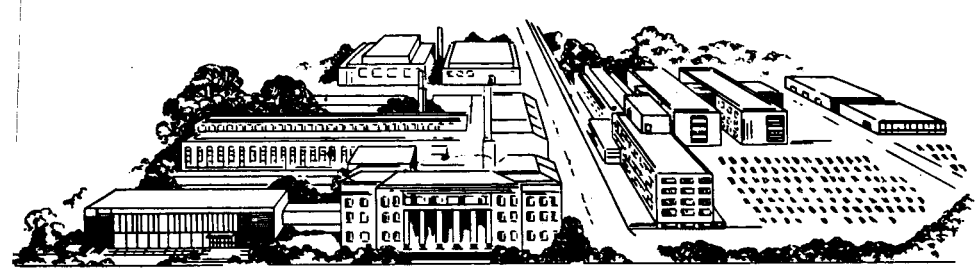
by

J. McCallum, G. R. Schaer, D. G. Trevethan, and C. L. Faust

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Contract NAS 3-6003



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THIRD QUARTERLY PROGRESS REPORT

on

DEVELOPMENT OF LARGE-INTERNAL-SURFACE-AREA
NICKEL-METAL PLAQUES

(Period Covered: December 19, 1964, through March 18, 1965)

April 8, 1965

by

J. McCallum, G. R. Schaer, D. G. Trevethan, and C. L. Faust

Contract NAS 3-6003

Prepared for

NASA-LEWIS RESEARCH CENTER
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DEVELOPMENT OF LARGE-INTERNAL-SURFACE-AREA NICKEL-METAL PLAQUES

by

J. McCallum, G. R. Schaer, D. G. Trevethan, and C. L. Faust

INTRODUCTION AND OBJECTIVES

As stated in the First Quarterly Progress Report, the specific objective of this program is the development of porous nickel-metal plaques for the rechargeable cadmium electrode to provide higher energy output per unit of weight than is presently available. To achieve this specific objective, the research has three general objectives:

- (1) Explore the possibilities for stacking electroformed screens into plaque structures with a uniform pore distribution
- (2) Control pore shapes by selective electroforming and stacking procedures
- (3) Demonstrate the physical and electrical advantages for the controlled pore shapes in nickel plaques.

During the first half of contract work, the feasibility was established of stacking electroformed screens into plaque structures with a uniform pore distribution. Characterization of commercial materials was completed to provide references with which to compare new electrode structures.

During this third quarter of work, the objectives were as follows:

- (1) Complete the fabrication of experimental electrodes for electrochemical evaluation
- (2) Identify ways to impregnate the experimental electrodes with active cadmium compound
- (3) Electrochemically evaluate the experimental electrodes.

Within each of these objectives for the third quarter, there are subsidiary objectives that will be apparent in the description of each task of the program.

SUMMARY

Porous experimental electrodes with straight-through holes have been made with three shapes of pores, four different size holes, and four different thicknesses.

Nineteen electrodes, each 1 cm x 1 cm, have been selected for experimental studies. These 19 electrodes are believed to be sufficient to study the effects of pore size, pore shape, electrode thickness, current density, and depth of discharge on energy output and on energy input. A stripping method that uses chromic acid will permit multiple use of the electrodes.

Porosity of these electrodes was increased up to 66 percent by chemically dissolving metal from the stacked and bonded screens. Higher porosities are possible, but porosities in the range of 60 percent were deemed adequate for the electrochemical evaluations.

Impregnation studies with the new experimental electrodes showed that a spongy cadmium metal could be electrodeposited within the straight-through pores. One such electrochemical impregnation is equivalent to four cycles of the more conventional chemical impregnations, on a basis of weight gains or percentage of pore volumes filled.

Chemical impregnation of stacked-screen electrodes, by an eight-cycle process, led to a greater percentage of pore volumes filled than was observed with commercial battery plaques. However, the subsequent electrochemical discharge showed the material to be less efficiently utilized from the screen electrodes.

A material-balance study of active materials in the negative electrode has shown that elemental cadmium is not always completely oxidized. The consequences are (1) discharge efficiency becomes less with each cycle and (2) impregnation procedures for commercial plaques are unsatisfactory for stacked-screen plaques.

FUTURE WORK

Details of future work plans are given for each task in the pertinent sections of this report. In brief, the planned work is aimed toward the following accomplishments during the next report period:

Task B - Porous-Mat Manufacture

An upper limit of porosity that can reasonably be obtained by etching stacked screens will be determined.

Task D - Plaques Classification

Physical properties of stacked-screen electrodes will be compared with commercial electrodes.

Task E - Impregnation Procedure

A procedure for impregnating screen plaques with a form of cadmium having reproducible activity will be selected.

Task F - Electrochemical Evaluation

Electrochemical evaluation of experimental plaques prepared on Task B will be commenced.

Task G - Corrosion Stability

Corrosion rate of sintered porous powder plaques and stacked-screen plaques will be compared.

EXPERIMENTAL WORK BY TASKS

The First Quarterly Progress Report itemized and discussed the research on each task as listed in the contract. The sections that follow are arranged in accordance with that format. Only new data and discussions are given in this quarterly report.

Task A - Raw-Material Classification

This task was completed and described in the First Quarterly Progress Report, pages 4-13. Classification of experimental plaques will be continued as part of Task D.

Task B - Porous-Mat ManufactureObjectives

The objectives of this task are to

- (1) Develop laboratory methods for making nickel porous plaques with specified size, shape, and length of pores
- (2) Provide a variety of electrodes of different pore configurations for experimental study.

Item 1 - Thickness Range

Porous electrodes of four thicknesses have been made as follows:

<u>Pore Shape</u>	<u>Nominal Thickness, mils</u>
Parallel Sides	5, 10, 21, 35
Keyed Opening	5, 10, 21, 35
Staggered Taper	5, 10, 21

Table 1 contains actual thicknesses and porosities of plaques as attacked and after etching to control porosity.

TABLE I. THICKNESS AND POROSITY OF STACKED-SCREEN PLAQUES

Specimen	Pore Shape	Mesh Size, pores per inch	Number of Screen Layers in Stack	After Stacking and Bonding		After Etching and Rebonding	
				Thickness, mils	Percent Voids	Thickness, mils	Percent Voids
23B	Straight sides	250	17	5.5	39	5.0	59
30	Ditto	250	11	10.5	45	9.1	59
31	"	250	22	21	47	18.0	60.5
24	"	250	40	36	40	33.0	60
43	"	250	27	22.5	41	(a)	(a)
44	"	250	32	35.5	43	(a)	(a)
23A	"	500	17	7.6	30	7.1	66
32	"	500	21	11	41	9.2	66
35	"	500	27	10	40	9.0	66
27	"	500	45	22.0	43	17.4	60
33	"	500	87	32	42	28.4	62
26	"	750	16	5.0	46	4.2	59.5
34	"	1000	33	10	41	7.6	66
25	"	1000	10	3.2	38	3.0	65
38	Keyed	250	12	5.6	52	(a)	(a)
37	"	250	30	8.7	57	(a)	(a)
45	"	250	38	23.5	56	(a)	(a)
49	"	250	63	35.5	53	(a)	(a)
48	Staggered taper	250	7	5.3	50	(a)	(a)
47	Ditto	250	15	11.0	48	(a)	(a)
46	"	250	29	20.5	50	(a)	(a)

(a) These mats were not etched to increase porosity by the end of this reporting period.

Item 2 - Technique for Making Mats

Stacking Screens. Screens have been stacked with superimposed holes by:

- (1) Using the stacking machine described on page 18 of the First Quarterly Progress Report
- (2) Positioning one screen at a time and fixing this screen in place by spot welding at the corners.

The precision with which screens were superimposed by using the stacking machine was improved greatly in this report period. Near perfect alignment was obtained in the latest plaques. Stacks of screens over 35 mils thick have straight-through holes, and light can be seen through these holes. Figures 1 and 2 are photomicrographs taken perpendicular to the surface of a 35.5-mil-thick screen plaque with both front-surface lighting and back lighting. The square, white areas are the holes with transmitted light. Note that the holes are nearly as large as the openings in the top screen, thus indicating nearly perfect alignment.

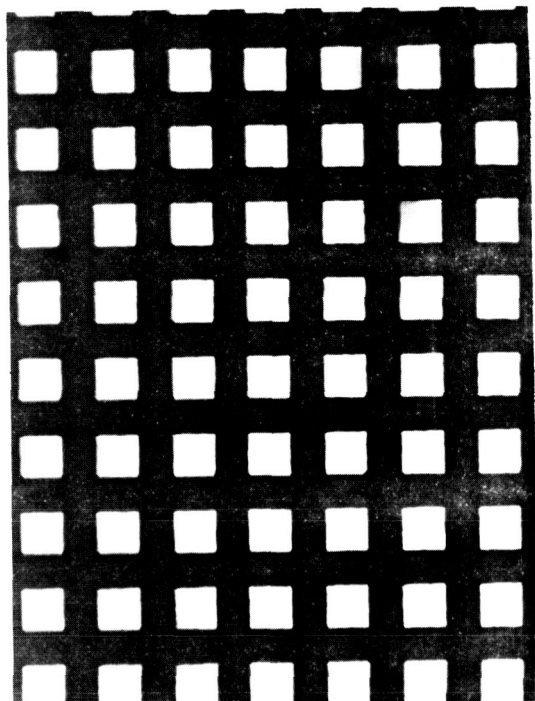
These improvements in alignment were obtained by a combination of

- (1) Better matching of die and punch sizes
- (2) Lighting of the stack from the back to provide constant monitoring of alignment while stacking
- (3) Improved operator skill.

The alignment of these stacked-screen plaques is better than the most optimistic prediction made before this work was started.

Electroformed screens 1 in. x 2 in. were superimposed by a new technique. Screens were positioned and spot welded one at a time to make a 6-mil-thick stack. Bonding of these screens to make a porous plaque was done in the usual way by heating to 1950 F in a hydrogen atmosphere. A cross section of this plaque is shown in Figure 9 in section Task E. Positioning was done by fastening the first screen to a piece of clear plastic with pressure-sensitive tape. A second screen was positioned over the first screen and shifted by hand until light could be seen uniformly through the screens. Clamps were then applied to hold the screens in register and the corners of the screen were spot welded. A third screen was positioned and welded the same as the second. Welding was done on the same spot on each layer by providing slots in the plastic just large enough for the bottom welding electrodes. Alignment of this first attempt at stacking screens by welding was not as good as obtained with the stacking machine. However, larger electrodes can be made this way and, by using a microscope to check positioning of each screen, improved alignment should be obtained.

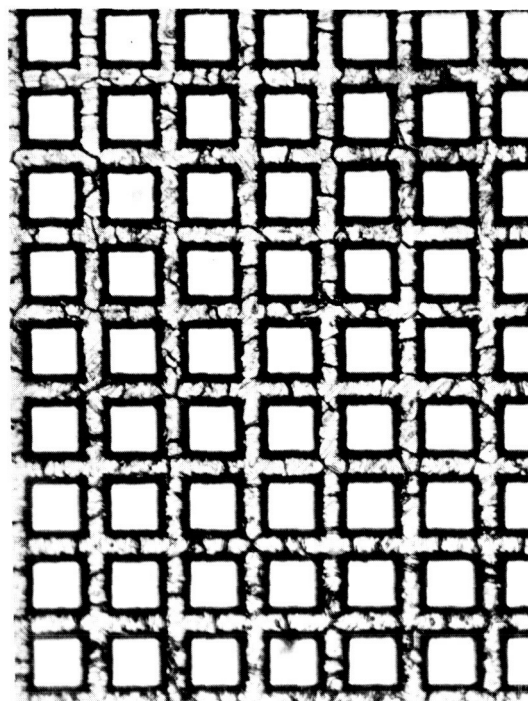
Electroforming Screens. Reusable mandrels for electroforming screens have been made and used. Holes were etched in copper panels, and the holes filled with glass as described on page 5 of the Second Quarterly Progress Report. The surface was polished to expose copper between the etched and filled holes; the copper surface



100X

FIGURE 1. SURFACE VIEW OF 250-MESH SCREENS CONTAINING 32 LAYERS STACKED TO 38.56-MIL THICKNESS BEFORE BONDING

Specimen lighted from the back only. White squares show openings through plaque. Specimen 44.



100X

FIGURE 2. SURFACE VIEW OF 250-MESH SCREENS CONTAINING 32 LAYERS AFTER BONDING TO 35.5-MIL THICKNESS

Both front surface and back lighting were used. White squares show openings through plaque. Specimen 44.

was chromium plated. One mandrel with glass-filled holes was used for electroforming 175-mesh nickel screens with a 2 x 4 inch area. After two screens were made, some of the glass pulled out of the holes. Apparently the glass cracked during polishing and nickel plated in these cracks, locking the nickel to the glass. Stripping the screen from the mandrel pulled the glass from the holes in the mandrels. Only the 175-mesh screen mandrel was used for electroforming. The 250- and 500-mesh mandrels were damaged during polishing to remove the excess glass. Polishing was done by hand rubbing with 600-grit silicon carbide abrasive on a rubber pad about 1/2 inch square.

Results with glass-filled copper mandrels has been moderately successful. Screens have been electroformed but the life was too short for practical use. This method could be developed for making long-life reusable mandrels. Reheating to flow the glass after polishing, to heal any cracks that were introduced, might give a long-life mandrel. No additional development work is planned for this mandrel system.

Another technique for electroforming screens was devised and one screen was electroformed to demonstrate that a screen can be reproduced by the process. A stainless steel sheet with holes etched through it was used as a master to make an electroforming mandrel. The mandrel had raised silicone rubber projections where the holes had been in the master screen. Figure 3 is a surface view of the mandrel showing the nonconducting, cone-shaped projections.

The procedure used was:

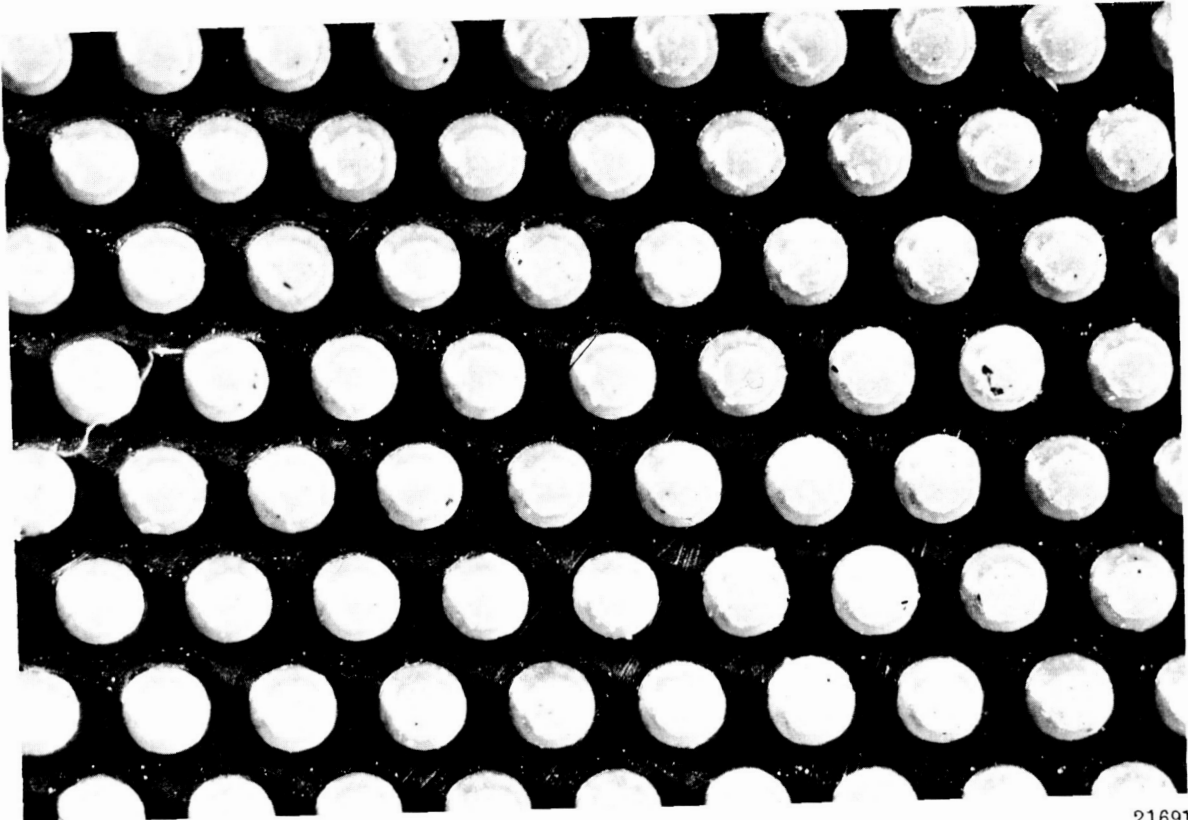
- (1) Fill the holes in the master screen with wax
- (2) Clean one side of the screen free of wax
- (3) Plate about 5 mils of nickel on the master
- (4) Remove the wax and fill the holes with silicone rubber* with an excess on the nickel-plated side and all excess doctored off the stainless steel side
- (5) Separate the nickel and the stainless steel screens after the silicone rubber hardened.

The resulting mandrel was a screen of electroformed nickel with rubber projections that duplicated the hole size and shape in the stainless steel masters.

A nickel screen was electroformed subsequently on the same mandrel that is shown in Figure 3. The resulting electroformed nickel screen duplicated the hole shape in the master stainless steel screen, as shown by the cross sections of the stainless steel master and the nickel electroform in Figures 4 and 5, respectively.

The screen size was about 50 mesh, which is coarser than the screens used in battery plaques. However, this master screen was available and easily could be used to check the process for reproducing holes with a preselected contour. Because the rubber cones pulled out of the electroformed nickel screen with no apparent damage,

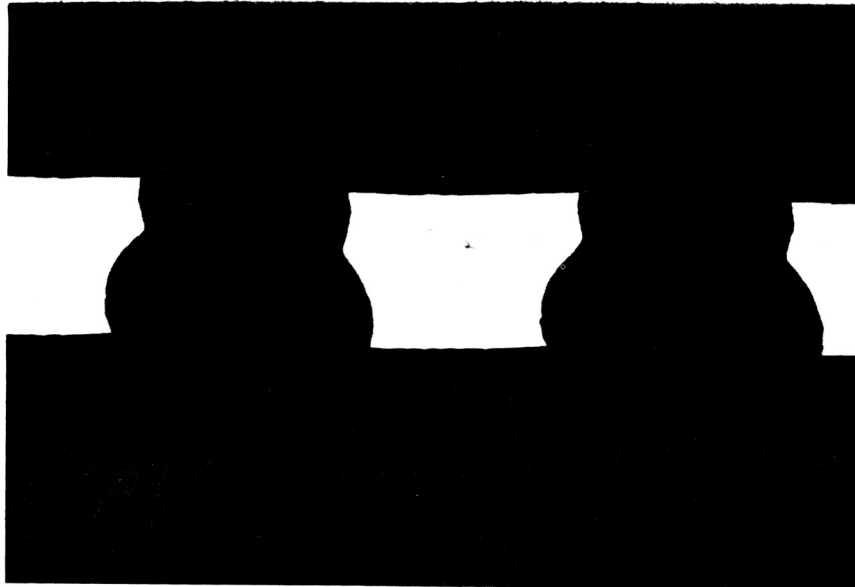
*Dow Corning Corporation, 502 Silicone Rubber.



30X

21691

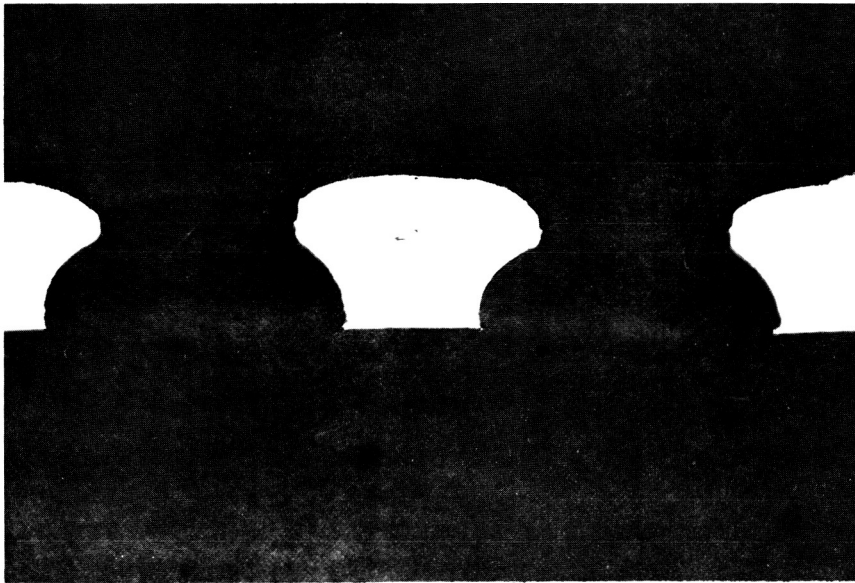
FIGURE 3. VIEW PERPENDICULAR TO SURFACE OF A NICKEL MANDREL (DARK AREA) WITH
CONE-SHAPED RUBBER PROTRUSIONS (LIGHT CIRCULAR AREAS)



100X

N21469

FIGURE 4. CROSS SECTION THROUGH HOLES IN MASTER STAINLESS STEEL SCREEN



100X

N21471

FIGURE 5. CROSS SECTION THROUGH HOLES IN ELECTROFORMED NICKEL SCREEN

Made with the mandrel in Figure 3 to duplicate the shape in Figure 4.
The bottom of the picture was the mandrel side.

the mandrel should be reusable. Electroforming of thick (1 to 5 mils) screens should be possible by this method without closing the holes. In contrast, present methods are limited in screen thickness obtainable because the holes close as plate thickness is increased.

Item 3 - Method for Controlling Pore Shapes

In prior work on this project two pore shapes were made, viz., parallel-sided and semirandom-shaped pores. In the work period covered by this report, plaques were made with keyed-opening-shaped pores and with staggered-taper-shaped pores, as required in the contract.

These two new pore shapes were obtained by stacking 250-mesh electroformed screens with different hole sizes. When two nickel screens are electroformed to different thicknesses, the thickest screen will have the smallest hole because the hole closes as thickness increases by electrodeposition. The keyed opening was obtained by stacking screens with 2-mil holes on the outside of the stack and screens with 3.2-mil holes in the middle. The staggered-taper pore was made by alternating screens with smaller and larger holes. Table 2 details the sizes of holes, thicknesses, and number of screens used to make these experimental plaques.

Control of Porosity. Plaques of stacked and bonded electroformed screens have porosities about half that of commercial sintered powder plaques. The commercial electroformed screens used in this work have wires more oval than rectangular in cross section. These screens, when made thick enough to support themselves, have openings of less than 50 percent. However, because of the shape of the wires, stacked and bonded screens have porosities greater than the percent open area. Most of the commercial screens that were stacked with superimposed holes had openings of 25 to 35 percent and the plaques made from these screens had porosities of about 40 to 50 percent.

A method was devised to etch stacked and bonded screens to increase the porosity to about 60 percent. Plaques were etched by trial and error until the desired porosity was obtained. After weighing and measuring the experimental plaques, the procedure used was:

- (1) Check weight and dimensions and calculate density and porosity
- (2) Rack the plaque with a spring clip made of nickel wire
- (3) Dip for 30 seconds in 50-50 mixture of concentrated hydrochloric acid and water
- (4) Rinse with water
- (5) Rinse with acetone
- (6) Dry by blowing with air
- (7) Immerse the plaque for 10 to 30 minutes in a solution containing 100 ml ethyl alcohol, 10 ml water, and 10 g iodine crystals

TABLE 2. CONTROL OF PORE SHAPE IN 250-MESH SCREEN PLAQUES

Specimen	Pore Shape	Thickness After Stacking and Bonding, mils	Screen-Stacking Sequence (a) Number of Layers and Percent Openings (b)
38	Keyed	5.6	2-25 : 8-50 : 2-25
37	"	8.7	2-25 : 26-50 : 2-25
45	"	23.5	3-25 : 31-50 : 3-25
49	"	35.5	4-25 : 55-50 : 4-25
48	Staggered taper	5.3	1-25 : 2-50 : 1-35 : 2-50 : 1-25
47	Ditto	11.0	2-25 : 2-50 : 1-35 : 2-50 : 1-35 : 2-50 : 1-35 : 2-50 : 2-25
46	"	20.5	3-25 : 3-50 : 1-35 : 3-50 : 1-35 : 3-50 : 1-35 : 3-50 : 1-35 : 3-50 : 1-35 : 3-50 : 3-25

(a) Number in table refers to number of screens and percent openings in the screens. Example: Specimen 38 had two screens with 25 percent open area, followed by eight screens with 50 percent open area, followed by two screens with 25 percent open area.

(b) Percent open area of screen corresponds to approximately the following hole sizes: 25 percent - 2.0 mils; 35 percent - 2.8 mils; 50 percent - 3.2 mils.

- (8) Rinse with acetone
- (9) Dry by blowing with air
- (10) Check weight loss and calculate new density and porosity
- (11) Recycle through Steps 2 to 9 until the desired porosity is obtained.

The etching solution, given in Step 7 of the procedure, removed about 1 mg of metal per minute from a 10-mil-thick plaque. The water in the solution increased the etch rate about 10 times over that of a pure alcohol solution of iodine. However, the surface finish was not quite as smooth as the one obtained in a nonaqueous etch. Too much water decreased the solubility of the iodine and promoted intergranular corrosion.

In a few experiments bromine was used in place of the iodine. Faster metal removal rates were obtained. However, the bromine-containing solution was not stable and the iodine solution is thereby the preferred etching solution.

Figures 6, 7, and 8, respectively, show surface views of stacked screens, heat-bonded screens, and chemically etched screens. The screens (Specimen 35 in Table 1) as stacked (Figure 6) show a regular pattern caused by the electroforming mandrel. After heat bonding, the screens (Figure 7) had an etch pattern that is referred to as a thermal etch. Some of the mandrel pattern was lost. After etching to increase porosity (Figure 8), all of the mandrel pattern had disappeared and some of the thermal etch lines had been removed.

Etching of screen plaques with the iodine-containing solution is considered to be a significant accomplishment for the making of porous electrodes with straight-through holes. Porosities of 66 percent were made in this work period (see Table 1). Higher porosities should be possible by this etching method.

Future Work

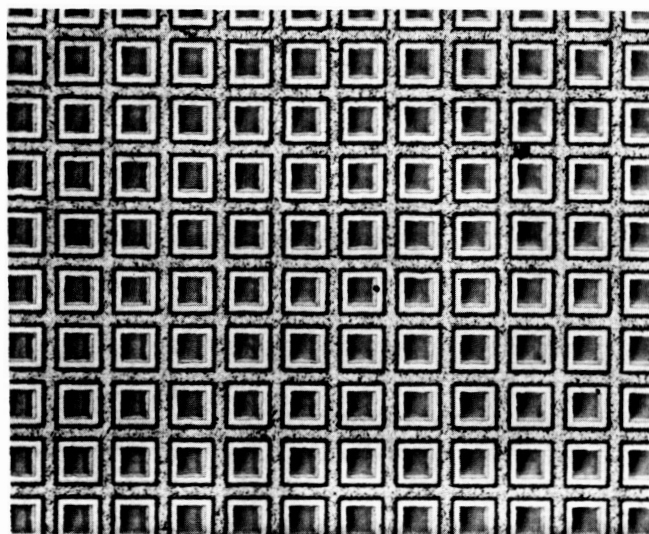
- (a) Stacking of 1 x 4-in. 250-mesh screens will be attempted to provide plaques for tensile-strength determinations.
- (b) Stacked and bonded screens will be etched to determine maximum porosity obtainable and still have reasonably stable structure.

Location of Data

All experimental data on Task B are contained in Battelle Laboratory Record Books Nos. 21516, pages 51 to 66, and 21595, pages 24 to 49.

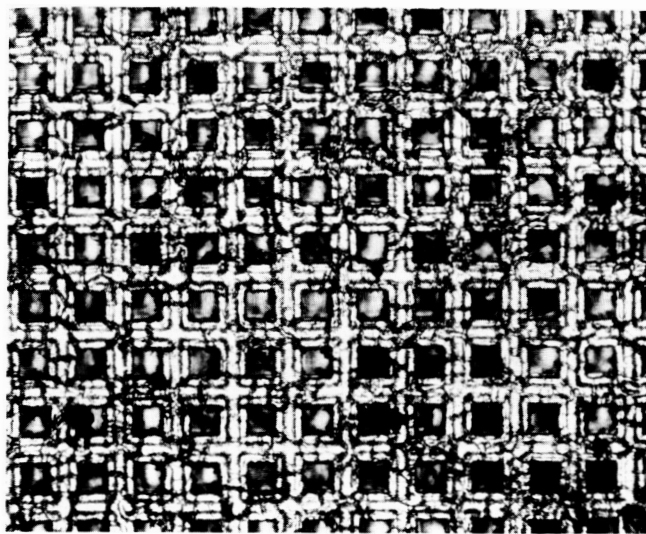
Task C - Sintered-Plaque Processing

The details of conditions selected for sintering stacked screens are given in the First Quarterly Progress Report, pages 19-21. These conditions will be modified only as needed to increase the quality of experimental electrodes.



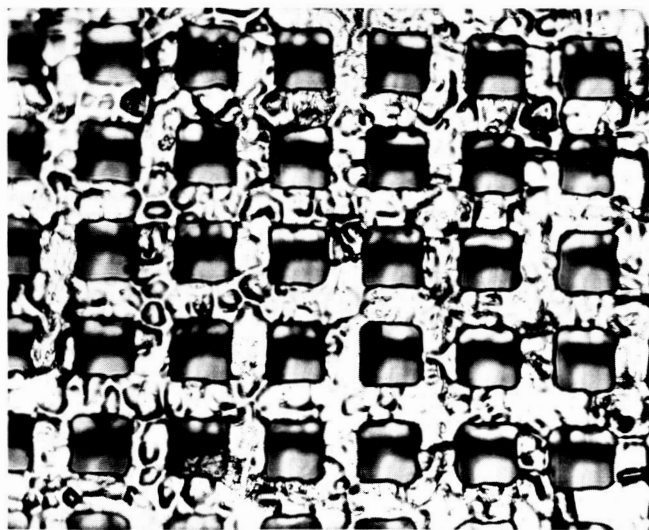
150X

FIGURE 6. SURFACE VIEW OF SUPERIMPOSED 500-MESH SCREENS BEFORE BONDING



150X

FIGURE 7. SURFACE VIEW OF SUPERIMPOSED 500-MESH SCREENS AFTER BONDING



250X

FIGURE 8. SURFACE VIEW OF SUPERIMPOSED 500-MESH SCREENS AFTER BONDING AND ETCHING

Task D - Plaque Classification

Eight physical properties of commercial sintered powder nickel plaques have been determined. These properties are summarized on page 12 of the Second Quarterly Progress Report. They will be used to compare results with selected stacked-screen electrodes.

Task E - Impregnation Procedure

Objectives

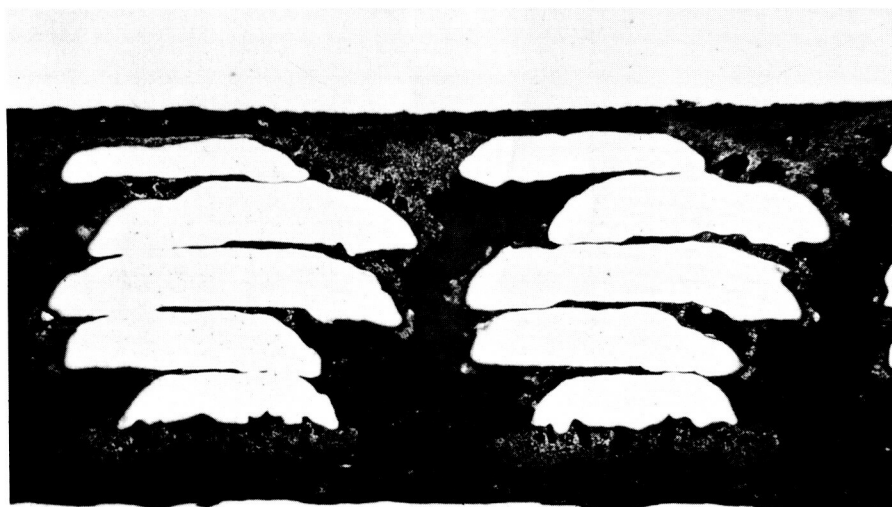
The main objective during this report period was to select the impregnation procedure which will be used for the evaluation of electrodes especially constructed for evaluation in Task F. A part of this objective was to evaluate a physical packing method of impregnation for comparison with chemical impregnation methods that are commonly used commercially.

Physical Impregnation of Screen Electrodes

Experimental screen electrodes were physically impregnated with cadmium by plating directly onto electrodes from a cadmium hydroxide slurry in 30 percent KOH solution. A current density of about 24 ma/cm^2 was used until a spongy coating of cadmium was visible. Usually this required about 2 hours at ambient room temperature. Excess material was physically rubbed into the pores. One such impregnation step gave a weight gain equivalent to having the pores 40 percent filled with $\text{Cd}(\text{OH})_2$. Four impregnation steps by the standard chemical impregnation procedures are required to yield the same percentage of filled pores.

Figure 9 shows a cross section of screens stacked by the spot-welding technique described in Task B. The white pattern in the figure is electroformed nickel screen. The darkest areas are unfilled voids. The lighter gray areas are the electrodeposited material that resulted from the physical impregnation procedure.

Prior to photographing Figure 9, the excess material on the top side of the electrode was rubbed into the pores. The bottom side of the electrode was untouched in order to indicate the thickness of the cadmium plated. The figure shows that cadmium fills the top entrance to the pore, but also that cadmium was plated directly on the wires within the pores. Since the quantity of cadmium plated on the surface was small compared with the pore volume, only a portion of the pore volume was filled. However, with sufficient cadmium plating on the surface and within the pores, the entire pore volume could be filled by this physical impregnation method because the pores are continuously straight through. This impregnation method will be unsuitable for the random-pore structure of powdered, sintered plaques, but would be desirable for straight-through pores because of its simplicity.



250X

20600

FIGURE 9. CROSS SECTION OF A PHYSICALLY IMPREGNATED STACKED-SCREEN ELECTRODE

Electrochemical Evaluation of Physical Impregnation

Following the encouraging weight gains obtained by the impregnation method just described, the next step was to evaluate the impregnated material to learn whether it was active. Early stacked screens, which were too thin for useful tests in Task F, were used for this evaluation of the new impregnations. Descriptive data are given in Table 3; the following conditions were held constant for each experiment:

- (a) All electrodes were impregnated as described in the previous section.
- (b) After impregnation, drying, and weighing, each electrode was charged at 2.4 ma/cm^2 to the hydrogen-evolution potential (Cycle 1 of the 250-mesh screen is a single exception as described later).
- (c) Discharge was at constant current at 9.6 ma/cm^2 to a voltage loss of about 0.1 volt from initial closed-circuit voltage.

The Cycle 1 discharge efficiency in the 250-mesh screen was made immediately after weighing the impregnated plaque without precharging. The apparent low efficiency value is evidence that the weighed material was partially oxidized. Therefore, all other discharge tests started after a charging step. The parenthetical value of 73 percent efficiency in Table 3 for Cycle 1 on the 250-mesh screen was estimated by increasing Cycle 2 efficiency in the same proportion observed for Cycle 2 to Cycle 1 for the 500- and 1000-mesh screens.

TABLE 3. DESCRIPTIVE AND EXPERIMENTAL DATA FOR PHYSICALLY IMPREGNATED SCREEN ELECTRODES

	Screen Mesh, lines/inch		
	250	500	1000
Cycle 1 Efficiency, percent	56.5 (73) ^(a)	70.5	63.2
Cycle 2 Efficiency, percent	60.10	57.3	53.0
Cycle 3 Efficiency, percent	50.7	50.0	45.8
Thickness, mils	2.0	2.1	3.0
Porosity, percent	42.1	39.8	34.0
Pore Volume Filled With Cd, percent	27.1	20.7	19.7
Maximum Pore Volume Filled With Cd(OH) ₂ , percent	63.8	48.7	46.3

(a) Estimated value.

The significant points to be noted in connection with Table 3 are these:

- (1) All the observed efficiencies are low relative to what was expected on the basis of Table 7, page 26, of the Second Quarterly Progress Report. Therefore, standard chemical impregnation was tried in the same thin plaques, as described in a later section.
- (2) Discharge efficiency decreased with each cycle. This effect suggested the need for new electrodes for each experiment. Therefore, means to clean impregnated electrodes were sought so that the same electrodes might be used several times, as described in the next section.

Removal of Cd/Cd(OH)₂ From Screen Electrodes

Notice in Table 3 that capacity losses occurred during deep cycling of the electrode. This cycling effect means that duplicate data may require using duplicate electrodes.

Solutions were evaluated that might strip cadmium and cadmium hydroxide from the screen electrodes without significantly attacking the nickel structure. Chromic acid solution, 200 g/l CrO₃, containing 10 cc H₂SO₄/l, removed cadmium from the negative electrode with no significant attack on the nickel structure. Chromic acid will dissolve both cadmium metal and cadmium hydroxide, so that the charge condition of the electrode is not important. Therefore, the active materials in a stacked-screen electrode can be stripped and the electrode can be reimpregnated for reuse.

Chemical Impregnation and Electrochemical Evaluation of Screen Electrodes

The physically impregnated electrodes were stripped with the chromic acid solution and were chemically impregnated four cycles per standard procedure. Discharge

data appear in Table 4 where the screens and conditions are those described in Table 3.

TABLE 4. EXPERIMENTAL DATA FOR CHEMICALLY IMPREGNATED SCREEN ELECTRODES

	Screen Mesh, lines/inch	
	500	1000
Cycle 1 Efficiency, percent	66.0	59.8
Cycle 2 Efficiency, percent	56.0	53.8
Cycle 3 Efficiency, percent	51.1	50.1

A comparison of Tables 3 and 4 shows that the physical impregnation of thin stacked-screen electrodes is nearly identical with the standard chemical impregnation. The result suggests that conventional impregnation procedures might have to be modified for the open-pore structures of the thin experimental screen electrodes. However, before judging whether to change impregnation procedures, it was thought desirable to continue studies with the standard procedure using thicker electrodes.

It was recognized also that up to eight chemical impregnation cycles might be required to compensate for porosity values. Table 5 shows results with stacked screens selected from those described in Table 1 after eight impregnation cycles. After the weight measurements of the eighth impregnation, the electrodes were charged at a current density of 4.8 ma/cm² and then discharged at 9.6 ma/cm².

TABLE 5. DISCHARGE DATA FOR SCREEN ELECTRODES CHEMICALLY IMPREGNATED EIGHT TIMES

Specimen	Screen Mesh, lines/inch	Thickness, mils	Porosity, per cent	Weight of Impregnated Cadmium, mg	Pore Volume Filled, percent	Discharge, mamp-hr	Discharge Efficiency, percent
23B	250	5.0	59	15.8	65.3	3.2	42.8
30	250	9.1	59	26.6	69.7	6.1	48.3
31	250	18.0	60.5	59.4	69.5	15.6	55.1
24	250	33.0	60	109.5	59.0	30.9	59.3
27	500	17.4	60	61.4	63.0	16.0	55.0
34	1000	7.6	65.5	28.1	68.3	6.7	59.9

The third and last columns in Table 5 show that efficiency of the negative electrode increased with electrode thickness. Screens with the smaller pores also show a greater efficiency. But even the best discharge efficiencies remained lower than desired for lightweight electrodes.

To see whether the relatively low efficiencies of Table 5 might be associated with the more than four standard chemical impregnations, commercial electrodes were evaluated with extra chemical impregnations.

Effect of Multiple Chemical Impregnations
on Energy Output

Commercial-battery plaques were used to determine the effect of additional chemical impregnations on discharge capacity. The plaques used initially had 44.7 percent of their pore volumes filled with cadmium hydroxide as reported on page 24 in the Second Quarterly Progress Report. They are believed to have had four impregnation cycles prior to assembly in the battery. These plaques were then given 0, 1, 2, and 3 additional chemical impregnation cycles. The charging current density used was 4.8 ma/cm² and the input capacity was just equal to the theoretical capacity of the plaques. All plaques were then discharged at a current density of 9.6 ma/cm² until a potential decrease of 0.1 volt from open-circuit voltage was reached. After an electrochemical evaluation of energy output, each sample was given one additional chemical impregnation and retested. The percentage of the pore volumes filled with cadmium hydroxide was calculated from the weight gains after each additional impregnation. The experimental results are given in Table 6.

TABLE 6. ENERGY OUTPUT AS A FUNCTION OF PERCENTAGE OF PORE VOLUME FILLED WITH Cd(OH)₂ FOR COMMERCIAL ELECTRODES

Specimen	Number of Additional Impregnations	Estimated Total Impregnations	Pore Volume Filled, percent	Efficiency, percent	Watt-Hours / Pound
S-4	0	4	44.7	73.2	69.5
S-5	0	4	44.7	74.4	70.8
S-3	1	5	50.0	80.3	80.4
S-1	2	6	50.6	88.5	89.1
S-2	3	7	54.8	81.2	85.0
S-4	1	5	49.8	77.7	79.5
S-3	2	6	54.2	78.3	82.5
S-1	3	7	54.3	82.4	84.6
S-2	4	8	55.0	77.7	81.3

Comparison of efficiencies for commercial electrodes in Table 6 with the efficiencies for screen electrodes in Table 5 shows the greater efficiencies for the commercial electrodes. Table 6 also suggests a trend of increasing efficiency with increased impregnation. However, if exception is made to the two blanks, Samples S-4 and S-5, there seems to be little effect of increased percent of pore volume filled upon the discharge efficiency.

The greater efficiency with powder plaques is attributed to the effect of geometry on the impregnation process rather than the effect of geometry on the discharge process. This interpretation follows because elemental cadmium build-up can be associated with discharge inefficiency, as described in the next section. The standard

chemical impregnation process of sintered powder plaques yields cadmium hydroxide, which is the objective. The same impregnation process of stacked screens yields cadmium metal. Thus, referring again to Table 5, the screens with the longer pores or with the smaller diameter pores show the greater discharge efficiencies because they were impregnated with less inactive cadmium metal. This statement implies that inactive cadmium is more easily deposited in large and easily accessible pores.

Energy-Output Efficiencies

The discharge efficiencies in Table 5 are less than 60 percent for screen electrodes but in Table 6 are greater than 75 percent for sintered powder electrodes. The data seemed to show that impregnation was yielding cadmium metal in the screens but cadmium hydroxide in the powdered plaques. A part of the cadmium metal so deposited within the screens is not available for discharge. With these observations and ideas in mind, a material balance was determined for the above discharged screens.

Assuming NaCN dissolves $\text{Cd}(\text{OH})_2$ without any attack on the nickel plaque or on the contained cadmium metal, it should be possible to determine the percentage of each contained material in the plaque. The distinction between metal and hydroxide is important because one can account for efficiency changes either by assuming cadmium metal build-up during discharge or by assuming cadmium hydroxide build-up during charge. Table 7 shows results with two of the plaques from Table 5.

TABLE 7. MATERIAL BALANCE OF DISCHARGED-SCREEN ELECTRODES

How Obtained	Item	Screens, lines/inch	250	1000
			Specimen 23B	34
Observed	1	Final plate weight after discharge, mg	58.7	82.4
Observed	2	Initial plaque weight, mg	40.7	50.3
1 - 2 =	3	Final weight of contained materials, mg	18.0	32.1
Observed	4	Experimental ma-min discharge capacity	194	402
Calculated from 4 =	5	Weight of $\text{Cd}(\text{OH})_2$ formed on discharge, mg	8.72	18.25
3 - 5 =	6	Calculated cadmium weight remaining after discharge, mg	9.18	13.85
Observed	7	Weight of material stripped by NaCN [probably $\text{Cd}(\text{OH})_2$], mg	12.2	21.5
7 - 5 =	8	Excess weight loss by NaCN strip	3.38	3.25
3 - 7 =	9	Weight of material remaining (probably cadmium metal), mg	5.8	10.6

In Table 7, Item 2 is the weight of starting electrodes before the eight impregnation steps. Item 4 is the ma-min discharge capacity observed and used for calculating the discharge efficiencies in Table 5. Item 1 is the dry weight after the discharge in Item 4. Item 3 is the numerical difference between Items 1 and 2 so that Item 3 contains cadmium and cadmium hydroxide, the proportions of which are unknown.

From Item 4, one can calculate the minimum amount of cadmium hydroxide using Faraday's law, as was done for Item 5. The difference between Items 3 and 5 is, therefore, the weight of unidentified material, either Cd or Cd(OH)₂, as given by Item 6. Item 7 shows the observed weight losses by a sodium cyanide leach. Notice that the weight losses of Item 7 are a little larger than the expected weight losses based on Item 5, as shown in Item 8. The important point is that Item 9, which is presumed to be cadmium metal, accounts for the majority of unidentified weight of Item 6. This is the important point because Item 9 implies that a substantial amount of cadmium metal remains in the electrodes after complete discharge.

Further work with Specimen 23B confirmed cadmium build-up as the cause of the observed low discharge efficiencies. After the NaCN strip, Item 7 of Table 7, the electrode was discharged without prior charging. The material undissolved by the NaCN yielded an additional 77 ma-min of discharge capacity. Based on the 5.8 mg of Cd metal, Item 9, discharge efficiency was about 46 percent, in good agreement with the original efficiency of about 43 percent. It is apparent that the Cd(OH)₂ stripped by the NaCN solution was "insulating" the cadmium metal thus preventing further discharge capacity.

Future Work

Experiments are planned to determine the necessary conditions for chemically impregnating stacked-screen electrodes. A better understanding of the impregnation and subsequent steps will be sought so that results might be properly interpreted and improved.

Location of Data

All experimental data on Task E are contained in Battelle Laboratory Record Books Nos. 21685, pp 75-83, and 21981, pp 20-56.

Task F - Electrochemical Evaluation

This task was temporarily postponed during this report period until a reproducible procedure of impregnation can be selected. All the needed electrodes are prepared as described in Task B of this report. Reference values on commercial electrodes are available in the Second Quarterly Progress Report, Task F, pp 14-40. Future work will demonstrate experimentally the effects of electrode geometry on electrode performance.

Task G - Corrosion Stability

The objective of this task is to demonstrate the difference, if any, in corrosion rates of sintered powder-nickel plaques and stacked-screen electrodes. Work will commence during the next report period using potentiostatic corrosion techniques on (a) flat nickel foil, (b) commercial sintered powder plaques, 21 mils thick, and (c) 250-mesh stacked-screen plaques, 21 mils thick.

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