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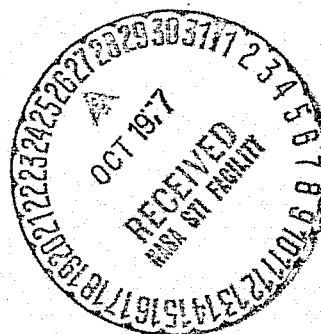
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PASADENA, CALIFORNIA

REVIEW OF ELECTROCHEMICAL IMPREGNATION  
FOR  
NICKEL CADMIUM CELLS

By Sidney Gross  
Electrical Power Technology

August, 1977  
JPL Contract 953984, W.O. 342-46

BOEING AEROSPACE COMPANY  
Seattle, Washington

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## ACKNOWLEDGEMENT

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## ABSTRACT

Electrochemical impregnation is a relatively new method of loading active material within the electrodes of nickel cadmium cells. When properly made, such electrodes are superior in energy density, stability and life, and appear to be especially well suited for aerospace applications. This technology has been reviewed and illustrated with typical performance data. Recommendations are made for additional research and development that would be useful in improving understanding and in further developing this technology.

## KEY WORDS

Aerospace batteries  
Batteries  
Cadmium electrode  
Electrochemical impregnation  
Electrochemical deposition  
Electrochemical loading  
Electrochemical processes  
Nickel cadmium batteries  
Nickel cadmium cells  
Nickel electrode  
Sealed cells  
Secondary batteries

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## 1.0 INTRODUCTION

### Definitions

Many processes for making nickel or cadmium electrodes employ electrochemical operations. For example, in the vacuum impregnation process nickel nitrate or cadmium nitrate is coated on the nickel sinter surfaces, then electrolytically converted to hydroxides in an alkaline solution. In such a process, the chemical compounds are already on the nickel sinter surfaces when electrochemical conversion commences. Thus, this step of the vacuum impregnation process is referred to as "electrochemical conversion".

In electrochemical loading processes, the active material originates in the electrolyte solution, and by electrochemical action is simultaneously converted and transported to the electrode surfaces. In this discussion, we distinguish between two types of electrochemical loading. "Electrochemical impregnation" refers to processes in which the pore surfaces of a sintered plaque are coated with active material by electrochemical means. Both nickel and cadmium electrodes can be made this way. "Electrochemical deposition" is used for processes in which, starting with a conductive substrate such as nickel screen, a porous electrode structure is built up electrochemically. Cadmium electrodes have been made this way, building up porous cadmium metal electrodes that require no additional active mass to function.

### Basic Electrochemical Impregnation Process

The basic process flow sheet for electrochemical impregnation of nickel and cadmium electrodes is shown in Figure 1.1. Detailed steps associated with these basic operations have been omitted in order to emphasize the main steps.

Sintered nickel plaques are placed opposite counter electrodes in a hot aqueous solution of nickel nitrate and nitric acid. Current is applied such that the plaque is made the cathode (reducing process), whereupon the desired metal hydroxide precipitates and deposits on surfaces within the plaque. After formation charge-discharge cycles the impregnation process is complete.

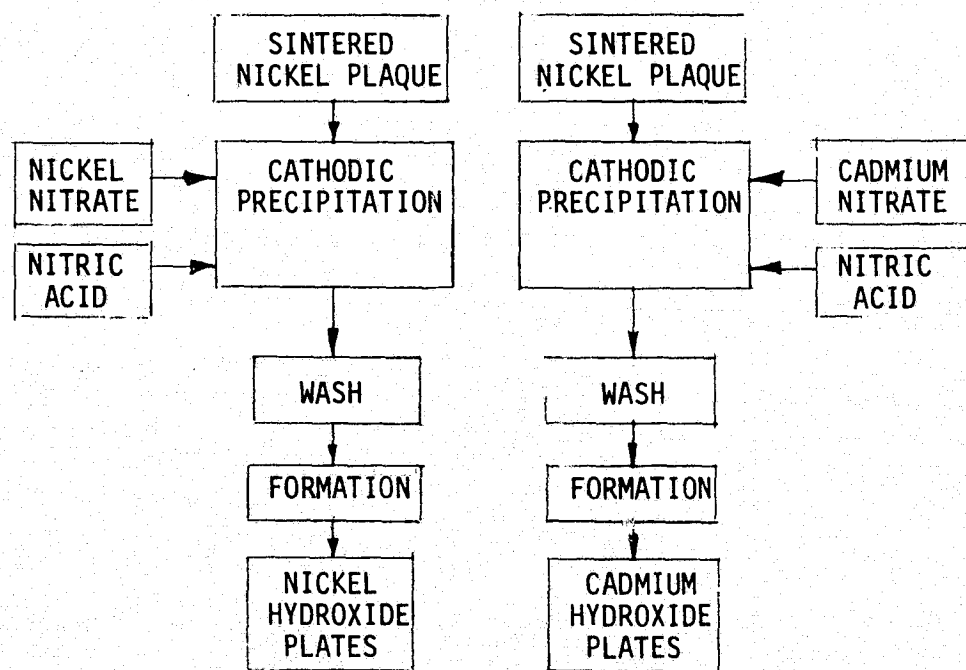


FIGURE 1.1 SCHEMATIC OF ELECTROCHEMICAL IMPREGNATION PROCESS

## Basic Principles

Nickel and cadmium electrodes are commonly made by the chemical impregnation method. With that process, the nickel sinter plaques are dipped into an acidified aqueous solution of nitrate salts, sometimes while under vacuum. The cadmium nitrate in the negative plates and the nickel nitrate in the positive plates are then converted to hydroxides by reaction with sodium hydroxide. The amount of material loaded in one cycle is limited by the solubility of the nitrates, so at least five impregnation cycles are needed to get enough loading.

In the electrochemical method, the cadmium or nickel hydroxide is electrolytically deposited in the pores of the plaque. Using the electrode structure as a cathode, current is applied while the electrode is immersed in aqueous nitrate solution. Active material can be distributed uniformly on the surface of the pore walls, giving low resistance between the active material and the metallic conducting structure and providing good mobility of electrolyte and evolved oxygen. This kind of structure gives plates that not only can be loaded fast, heavily and repeatably, but which also operate more efficiently and are longer-lived than plates made by the conventional chemical impregnation method.

The important principle involved in electrochemical impregnation is that when current is applied reactions occur which remove hydrogen ions from solution, making the interior of the plaque less acidic. Nickel hydroxide or cadmium hydroxide precipitates when the pH rises to the precipitation pH value, which is approximately 7.0 for cadmium hydroxide (1) and about 5.0 for nickel hydroxide (2). The highest pH occurs deep within the plaque, farthest from

the surface, where diffusion is the slowest. Thus, precipitation starts in the interior and progresses toward the outside surface.

### Chemical Reactions

The chemical reactions which produce precipitates of active material are



and

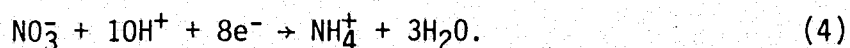


There are two processes occurring simultaneously in the plaque which remove hydrogen ions and thus increase the pH. These are hydrogen evolution and nitrate reduction. Whether hydrogen evolves or not depends on the specific operating conditions, and it occurs by the following reaction:

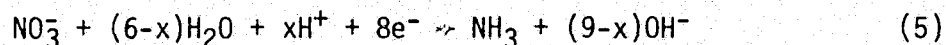


Hydrogen evolution requires a greater potential than does nitrate reduction, so hydrogen generation is limited mostly to high current density processes.

Nitrate reduction has commonly been considered to result in ammonia by the following reaction (3 and 4):

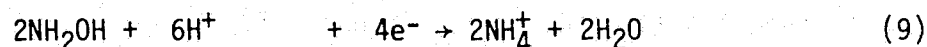
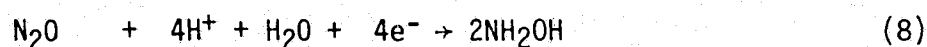
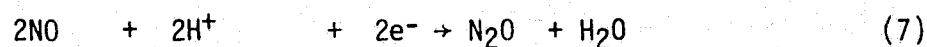
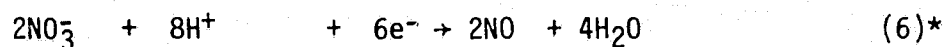


Seiger (5, 6, and 7) proposes a different form for this reaction, thus:



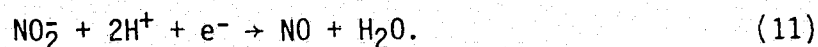
where "x" is an integer that is variable. Hausler (3), Seiger (5 and 6), and Takamura (4) have verified that ammonia is formed by reduction of nitrate, and Hausler's experiments (3) showed that the amount of ammonia formed was 87 percent of theoretical.

There are a host of other reactions which are thermodynamically possible and which may also occur. Hausler suggests that nitrate reduction according to reaction (4) takes place in the following partial steps:

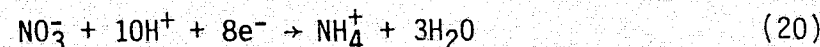
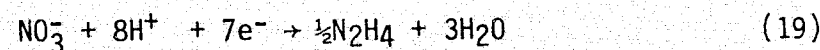
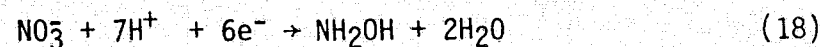
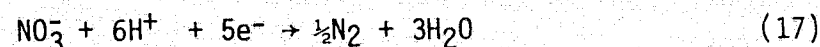
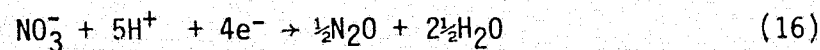
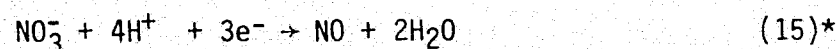
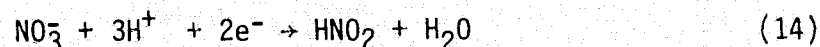
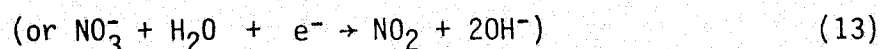
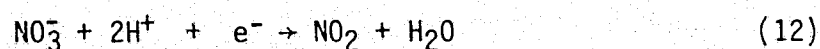


Reduction of nickel ion to nickel is also possible, but reduction of nitrate ion is a much more favored reaction, having a more positive redox potential (3).

Beauchamp (8 to 12) proposed that reaction (6) is a principle one, and with sodium nitrite added as a pH buffer, proposed the reaction:



Pickett (13) proposed the following reactions as being possible at the nickel or cadmium cathode:



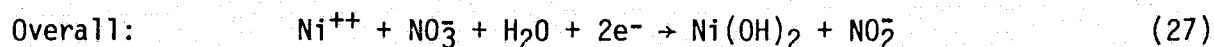
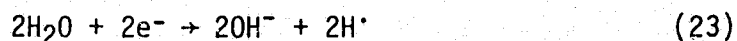
\*Equations 6 and 15 are functionally identical.



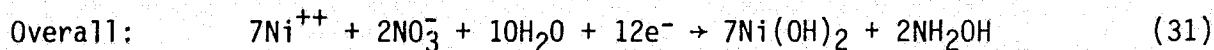
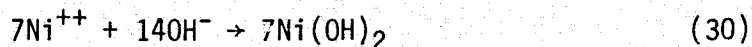
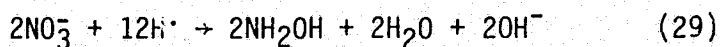
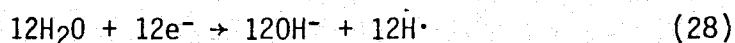


MacArthur (25) considered four candidate reactions for the reduction of nitrate, two of which were essentially the direct reduction by means of reactions 14 and 15. The third and fourth reaction paths were the indirect reduction to nitrite and hydroxylamine, respectively, involving nascent hydrogen as an intermediate, thus:

Indirect reduction to nitrite:



Indirect reduction to hydroxylamine:



MacArthur concluded that the dominant mechanism is the indirect reduction to nitrite, reactions 23 to 27; this corresponds theoretically to two Faradays to one mole nickel hydroxide, and fitted his experimental data if the Faradaic efficiency were approximately 70 percent. He also concluded that alpha nickel hydroxide forms from the nitrate reduction, and then changes to the less hydrated beta nickel hydroxide which is not as efficient on discharge.

The opposite electrode, the anode, can either be an inert metal or consumable nickel or cadmium. With inert electrodes, such as titanium or platinum, oxygen gas and hydrogen ions are produced by the following reaction:



Consumable nickel or cadmium electrodes are sometimes used, providing a source of material for impregnation. These reactions are:

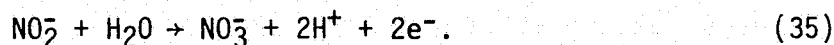


and



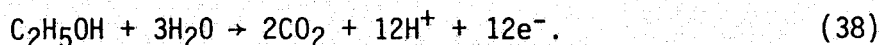
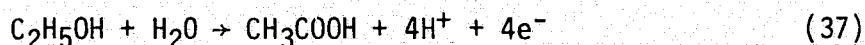
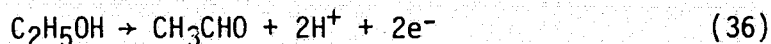
Some processes do not use consumable electrodes, but use nickel nitrate and cadmium nitrate instead as sources of material for impregnation.

In Beauchamp's process (8 to 12), sodium nitrite is added as a buffer to minimize pH changes in the electrolyte bath. The reaction is



Use of this buffer can prevent the generation of oxygen given by reaction 32.

The impregnation process developed by Pickett (13 to 20) has ethanol added to the nitrate solution. The ethanol reacts to generate hydrogen ions and minimize pH changes, oxidizing to acetaldehyde, acetic acid and carbon dioxide (13) as follows:



These reactions help stabilize hydrogen ion concentration in the electrolyte bath similar to the way this is done by nitrite ion per reaction 35.

### Loading Level Parameters and Units

A design variable of major importance is the level of loading to be used. The initial development work with this method resulted in loading limits for nickel hydroxide of about 1.2 grams/cc of void, whereas today loadings twice as large have been reached.

One problem confronting those reading the literature is that data are presented in a variety of ways, making it difficult to relate one test to another. Results have been reported in terms of ampere-hours per decimeter<sup>2</sup>, ampere-hours per cubic centimeter, ampere-hours per cubic inch, grams per square centimeter, grams per square inch, grams per cubic centimeter, and grams per cubic inch. Further confusion occurs when porosity and coining information are not given, or when the reported ampere-hours are not specified as either measured, or theoretical based on weight gain.

From a physical standpoint, grams of active material per cubic centimeter of void is preferred, for the sinter void volume after impregnation is partially occupied by active material. Thus, the theoretical upper limit of loading is the active material density, being for  $\text{Cd}(\text{OH})_2$  4.6 grams/cc, and for  $\text{Ni}(\text{OH})_2$  3.65 grams/cc in the green hydrated condition or 4.15 grams/cc when amorphous. Sometimes loading is expressed as a fraction of the void volume; thus, 2.3 grams/ $\text{Cd}(\text{OH})_2$  per cubic centimeter void volume would be loading to 50 percent of the void volume.

Loadings in grams/cc void may be converted to grams/cc by multiplying by the plaque porosity, typically about 0.80. From an application standpoint, it is also useful to determine ampere-hours delivered per unit volume and per

unit weight. The theoretical conversion factors are 0.289 Ah/gm of  $\text{Ni(OH)}_2$  and 0.366 Ah/gm of  $\text{Cd(OH)}_2$ . Loadings per unit area can be converted to unit volumes knowing plaque thickness, which typically is 0.030 inches. Since there is a loss of active material after formation and cleaning, the final weight gain must be used for performance calculations. Also, electrode swelling that occurs during impregnation and formation will alter the porosity and void volume, and this too must be taken into account.

Properties of coined edges are especially important for small cells, where they constitute a significant fraction of plate area. Effects of coined edges can be determined knowing geometry, pickup characteristics, and utilization. With chemical impregnation, coined edges typically pick up from 25 percent to 70 percent as much active material as the rest of the plaque, but little information is available on characteristics of coined edges under electrochemical impregnation.

The important characteristics needed to define electrochemically impregnated electrodes are listed in Table 1.1. Often many of these cell characteristics are not reported. Sample calculations are given to show typical use of this information. On research and development programs and important aerospace procurement programs, it is recommended that requirements be imposed to include data on these items.

TABLE 1.1: PARAMETERS REQUIRED TO DEFINE ELECTROCHEMICALLY IMPREGNATED ELECTRODES

PARAMETER	SAMPLE CALCULATION FOR NICKEL ELECTRODES		
	UNCOINED AREA	COINED AREA	ELECTRODE AVERAGE
Area Fraction	0.95	0.05	1.0
Sinter Thickness	0.030	0.020	0.030 in <sup>2</sup>
Sinter Porosity	80	30	77.5 percent
Sinter Void Volume	0.37	0.14	0.36 cc/in <sup>2</sup>
Loading Level	2.0	1.5	1.98 g/cc void
Weight Ni(OH) <sub>2</sub> loading	0.73	0.15	0.70 g/in <sup>2</sup>
Weight Ni(OH) <sub>2</sub> corrosion	0.01	0	0.01 g/in <sup>2</sup>
Weight Ni(OH) <sub>2</sub> total	0.74	0.15	0.71 g/in <sup>2</sup>
Weight Co(OH) <sub>2</sub>	0.05	0.01	0.048 g/in <sup>2</sup>
Theoretical capacity - 1 elec.	0.21	0.04	0.201 AH/in <sup>2</sup>
Formation capacity	0.23	0.04	0.220 AH/in <sup>2</sup>
Utilization	1.09	1.00	1.085
Sinter weight, initial	0.83	0.83	0.83 g/in <sup>2</sup>
Sinter weight after corrosion	0.82	0.82	0.82 g/in <sup>2</sup>
Grid weight	0.26	0.26	0.26 g/in <sup>2</sup>
Plate weight	1.88	1.24	1.85 g/in <sup>2</sup>
Capacity per unit weight	0.122	0.032	0.118 AH/g
Capacity per unit volume	7.67	2.0	7.38 AH/in <sup>3</sup>

## 2.0 ELECTROCHEMICAL IMPREGNATION EXPERIENCE

### Kandler's Work

Kandler first developed and explained the process for electrochemical impregnation of porous structure with the hydroxides of nickel and cadmium (Refs. 1,21,22). He recognized the need for ions such as nitrate which have a high redox potential that is more positive than that of nickel or cadmium, preventing deposition of those metals in the pores by reducing the nitrate instead. He also recognized the existence of a pH gradient which does not allow hydroxide to precipitate except deep within the pores where the pH is highest, causing the pores to be filled from the inside out. The option to use either inert or soluble anodes is also attributable to Kandler.

Kandler's process operated at room temperature in contrast to today's technology of 80 to 100°C (e.g., Ref. 13). Nickel electrodes are electrochemically impregnated in a solution of 10 percent concentration of nickel nitrate, with nitric acid added to obtain a pH of about 3. Nickel foil was used for a counter electrode (anode). Impregnation of 26 mil plaque required approximately five hours to reach a capacity of 1.5 AH/dm<sup>2</sup> (0.097 AH/in<sup>2</sup> and 3.73 AH/in<sup>3</sup>). Current density for two sides is estimated to be 0.027 A/in<sup>2</sup>, which is unusually low. To obtain high loadings, he used two or more stages of impregnation, drying the electrode between impregnation cycles.

Kandler's current density (0.027 A/in<sup>2</sup>) was very low compared with today's technology (typically 0.18 A/in<sup>2</sup> based on two sides). Another unusual feature was the fact that the active impregnating material was green bivalent nickel hydroxide (Ref. 22), in contrast with the black bivalent nickel hydroxide generally obtained today. The green form is more hydrated and less compact,

possible explaining the low energy density. Scanning electron micrographs, however, show the structure to be very high in area, very much resembling the appearance of a sponge. This may be due also to the production of green nickel hydroxide, for nickel electrodes made by other electrochemical impregnation methods do not show a similar structure.

A few percent of cobalt were used in Kandler's nickel electrodes, and also other undefined metallic additions (1). Kandler also showed that his nickel electrodes had such a high surface area that when reduced in hydrogen at high temperature they formed excellent porous metallic nickel electrodes (22).

Cadmium electrodes were impregnated in 80 percent cadmium nitrate solution kept at pH of about 1.0 with the addition of nitric acid. A sacrificial cadmium anode was used for the counter electrode. Capacity of an 0.026 inch thick electrode was 1 to 1.5 AH/dm<sup>2</sup> (0.0645 to 0.0968 AH/in<sup>2</sup>, and 2.48 to 3.72 AH/in<sup>3</sup>). For cadmium electrodes, Kandler apparently was successful with porous iron plaques as well as with porous nickel plaques (20).

Kandler produced nickel cadmium cells with lower internal resistance than conventional cells (1), and has reported the discharge voltage to be appreciably higher as a result (Figure 2.1). Though nitrate ions are especially well suited to this process, he also reported (21,22) that chromium acid ions, chlorate ions and permanganate ions could be used. Also, he was successful in impregnating nickel electrodes by substituting hydrochloric acid for nitric acid (22).

Basis:

- o Kandler, Ref. 1
- o Capacity = 3 AH
- o A = Electrochemical Impregnation
- o b = Chemical Loading
- o Discharge at 0.5 hr. 2.5 hrs, and 5.0 hrs.

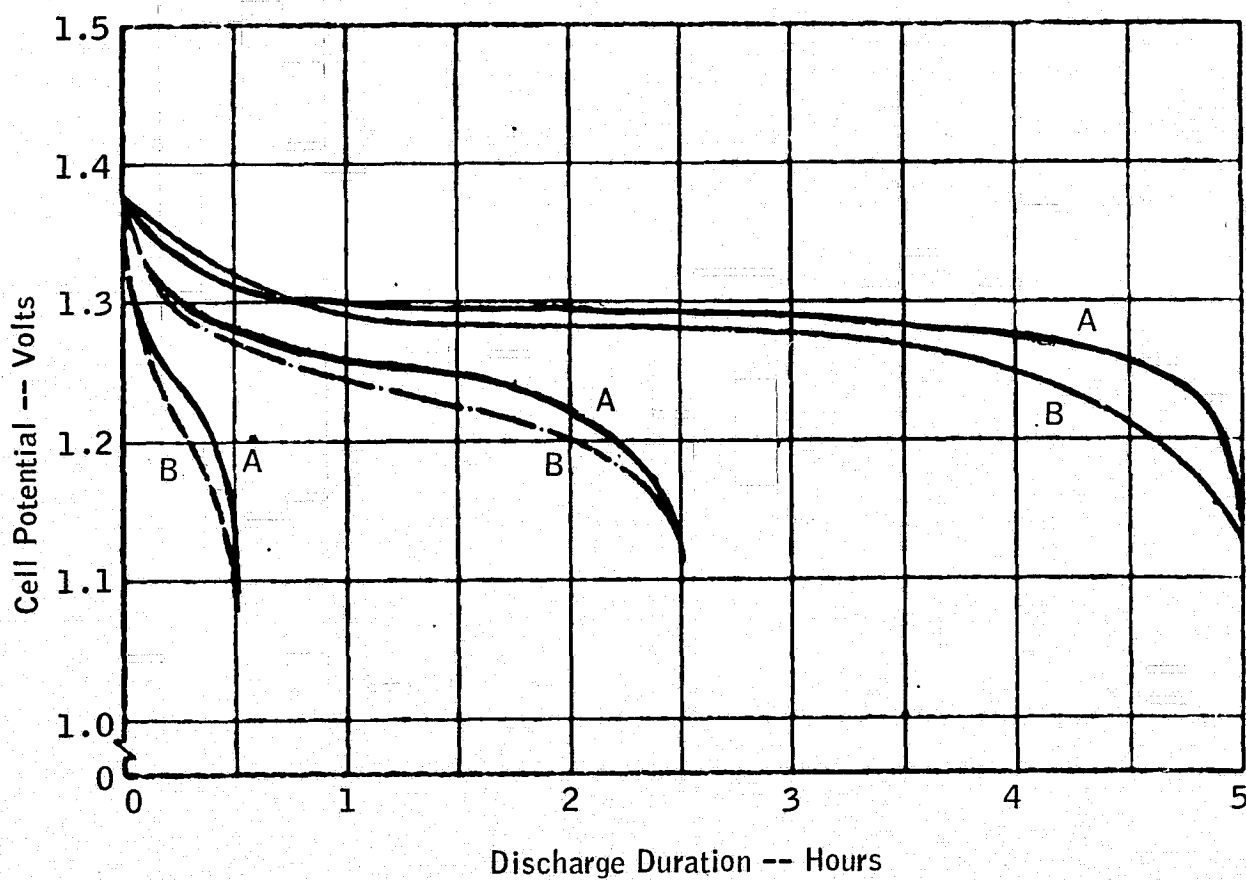


Figure 2-1: Effect of Chemical Loading versus Electrochemical Impregnation on Discharge of Nickel Cadmium Cells



### Hausler's Work

Some of Hausler's work was done in close collaboration with Kandler, and thus their results have some common features. Hausler's objectives included close control of capacity rather than maximum capacity. Using 1.15 mm (0.045 in) sintered nickel plaques of 79 percent porosity, his nickel electrode impregnations took 10 hours in 10 percent aqueous solution (0.29M) of nickel nitrate hexahydrate (3). Electrolyte pH is controlled between 2.0 and 3.0, current density is approximately  $0.5 \text{ A/dm}^2$ , and temperature is held at  $25^\circ\text{C}$ . Temperature was limited because even filling of the pores could not be guaranteed at higher temperatures, due to pore blockage. Also, he experienced grid corrosion at higher temperatures.

Capacity of these electrodes was  $1.65 \text{ AH/dm}^2$  ( $0.106 \text{ AH/in}^2$  and  $2.45 \text{ AH/in}^3$ ). Capacity could be made only about 10 percent greater for these plates without experiencing swelling. These plates were within a  $\pm 3$  percent capacity tolerance, however. Also, this technology was reduced to practice and used for mine lamp batteries.

Hausler has been able to impregnate nickel electrodes homogeneously up to a thickness of 5 mm (0.2 in). This is a remarkable achievement and clearly shows the unique capability of this process. His method produces green nickel hydroxide, which is probably related to his success.

Using a grid similar to that used for the nickel electrode, impregnation of cadmium electrodes was also done at pH 1.0 and required seven to eight hours. Sacrificial cadmium anodes were used in this method. Capacity for these electrodes was  $2.1 \text{ AH/dm}^2$  ( $0.135 \text{ AH/in}^2$  and  $3.01 \text{ AH/in}^3$ ) with a tolerance of

±3.3 percent. He found with cadmium electrodes that too high a current density would result in plating of cadmium metal rather than reduction of nitrate to ammonia.

Hausler recognized the importance of the plaque being highly reproducible with respect to porosity and pore structure. He also demonstrated the importance of pore structure. Pores should be funnel shaped, with greater cross-section area at the entrance than in the interior. Such plaques made by the slurry technique show this pore structure, due to the pore-forming effect of the vaporizing water. Pores with narrow openings are the worst kind for electrochemical impregnation, for diffusion is impaired and the openings can become plugged easily; compaction fabrication methods produce such pores. Pores with regular diameter are acceptable, though not ideal; loose sintering of dry powder produces a structure with relatively constant pore diameter.

#### McHenry's Work

McHenry (23,24) used 85 percent porous plaque 0.028 inches thick and obtained typical loadings of 1.2 g/cc of void for nickel electrodes. His work was carried out at 25°C at 0.55 A/in<sup>2</sup> with pH ranging from 0 to 2.8. The effect of time of impregnation on capacity and weight gain of active material is shown in Figure 2.2. Theoretically, the amount of active material should be proportional to the number of coulombs provided. However, the electrochemical efficiency of the material deposited in the first two minutes is seen to be less efficient than material subsequently deposited. This kind of trend is also observed in chemically impregnated nickel electrodes and appears to be characteristic of the nickel electrode. As the amount of active material is increased, pore size is reduced and mass transfer is impeded, causing a loading limit to be reached.

Basis:

- o Ref. 23
- o Electrodes 2.25" x 1.00" x 0.028"
- o pH 0 to 2.8
- o 4M  $\text{Ni}(\text{NO}_3)_2$  solution
- o 5.0 amperes
- o 25°C

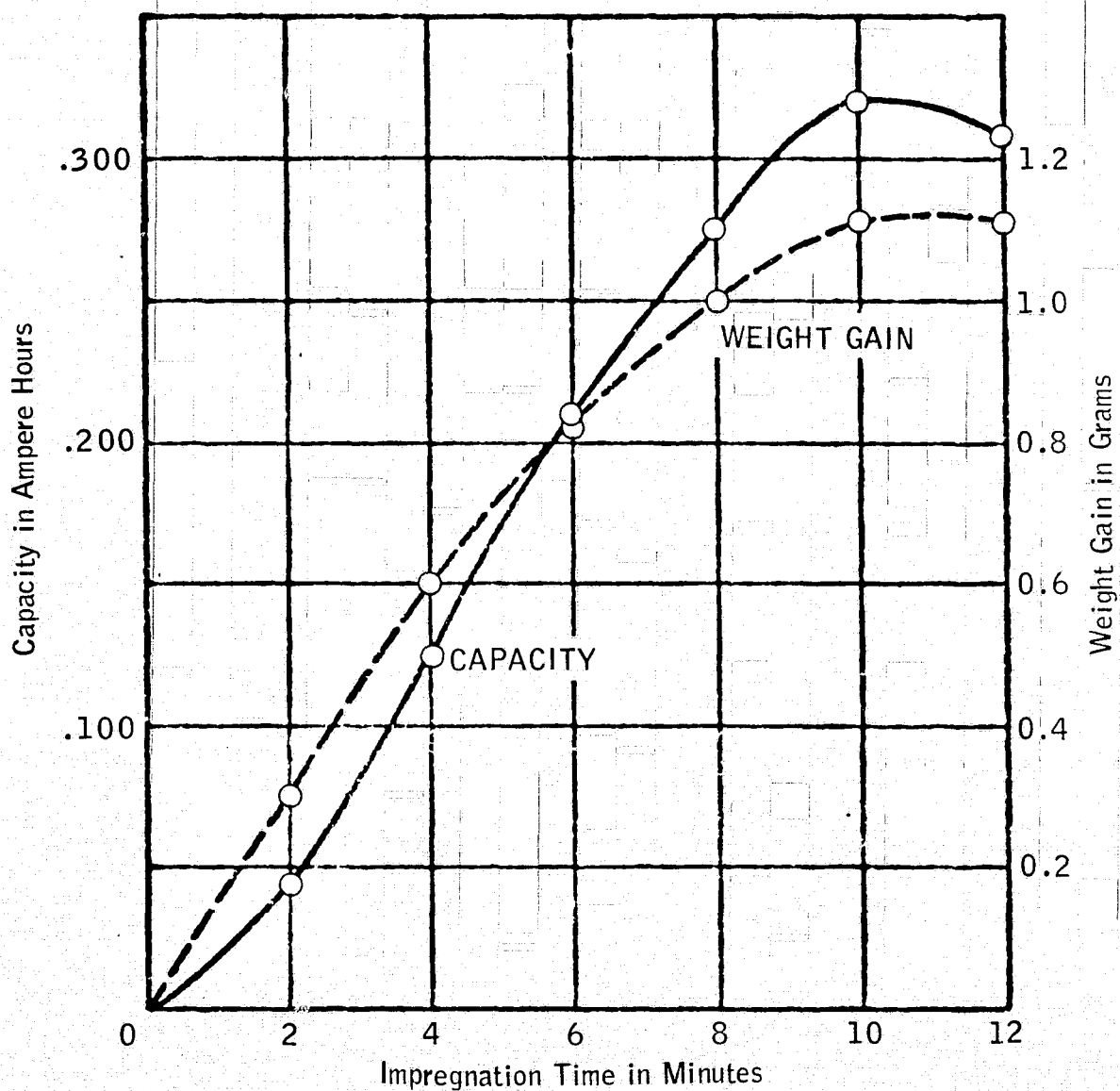


Figure 2.2: Electrochemical Impregnation Rate of Nickel Electrodes by McHenry

McHenry's data on the effects of current density, temperature and nickel nitrate concentration on loading are shown in Table 2-1. The number of coulombs passed through each electrode was kept constant; this restriction probably affected the results, for optimum test conditions could not have been reached in all cases. At first inspection, it would appear that the wide range of loadings and the absence of clear trends is due to poor reproducibility. This is not the case, however, for additional data shows that reproducibility was very good. The apparent explanation is that the loading is very sensitive to the specific operating conditions. Only certain precise combinations of conditions will give good loading. The maximum loading, not shown in this figure, was approximately 1.2 g/cc of void.

The efficiency of the electrodes produced by electrochemical impregnation is of concern in the development of lightweight cells. For some conditions, the efficiencies reported in Table 2-1 were greater than 100 percent, corresponding to more than one electron transfer. There was no clear trend on efficiency, however.

Accelerated cycling tests on McHenry's electrochemically impregnated nickel electrodes showed excellent stability (Figure 2-3). The electrodes used (Table 2-1) had a calculated loading of 0.9 g/cc of void. Features of the test cell included a negative to positive ratio greater than 2.0, electrolyte that was 4.3 M in KOH and 1.0 M in LiOH, Pellon nonwoven nylon type 2505 separator, and a cell assembly compression of 200 psi. The cycle consisted of a 6-hour charge at 0.150 amperes (C/3), an 0.5 hour open-circuit period, a discharge at 0.250 amperes (C/2) to 1.0 volt, and another 0.5 hour open-circuit period. Results (Figure 2-3) showed excellent stability to 192 cycles, with less than one percent change of capacity during this time.

TABLE 2-1: ELECTROCHEMICAL IMPREGNATION OF  
NICKEL ELECTRODES BY McHENRY

Basis:

- o Ref. 17
- o Electrodes 2.25" x 1.0" x 0.028"
- o 1500 coulombs per electrode
- o 100% efficiency corresponds to one electron transfer

CURRENT	TEMPERATURE	Measured Ampere-Hour Capacity (Measured Electrode Efficiency)		
		0.2 M Ni(NO <sub>3</sub> ) <sub>2</sub> pH = 2.8	1.0 M Ni(NO <sub>3</sub> ) <sub>2</sub> pH = 1.2	4.0 M Ni(NO <sub>3</sub> ) <sub>2</sub> pH < 0
0.2 Ampere (125 Minutes, 0.0069 A/cm <sup>2</sup> )	25°C	0.181 (1.24)	0.079 (1.00)	0.221 (1.09)
	50°C	0.172 (0.86)	0.145 (1.00)	0.144 (1.16)
	70°C	0.113 (0.68)	0.163 (1.10)	0.045 (1.05)
1.0 Ampere (25 Minutes, 0.0345 A/cm <sup>2</sup> )	25°C	0.040 (0.87)	0.234 (1.25)	0.186 (1.31)
	50°C	0.061 (0.74)	0.246 (1.22)	0.101 (1.15)
	70°C	0.047 (0.72)	0.239 (1.11)	0.083 (0.98)
5.0 Amperes (5 Minutes, 0.172 A/cm <sup>2</sup> )	25°C	0.033 (0.66)	0.062 (0.52)	0.224 (1.01) ▷
	50°C	0.036 (0.61)	0.132 (0.87)	0.228 (1.37)
	70°C	0.033 (0.75)	0.175 (0.95)	0.165 (1.22)

▷ Condition selected for subsequent tests.  
Calculated loading is 0.90 g/cc of void.

Basis

- o Electrolyte is 4.3 M in KOH, 1.0 M in LiOH
- o Nylon separator
- o Negative to positive capacity ratio 2.0
- o Cell compression = 200 psi
- o Charge: 6 Hrs at 0.15 A  
0.5 Hr open circuit
- o Discharge: 0.25 A to 1.0 V  
0.5 Hr open circuit
- o McHenry, Ref. 23

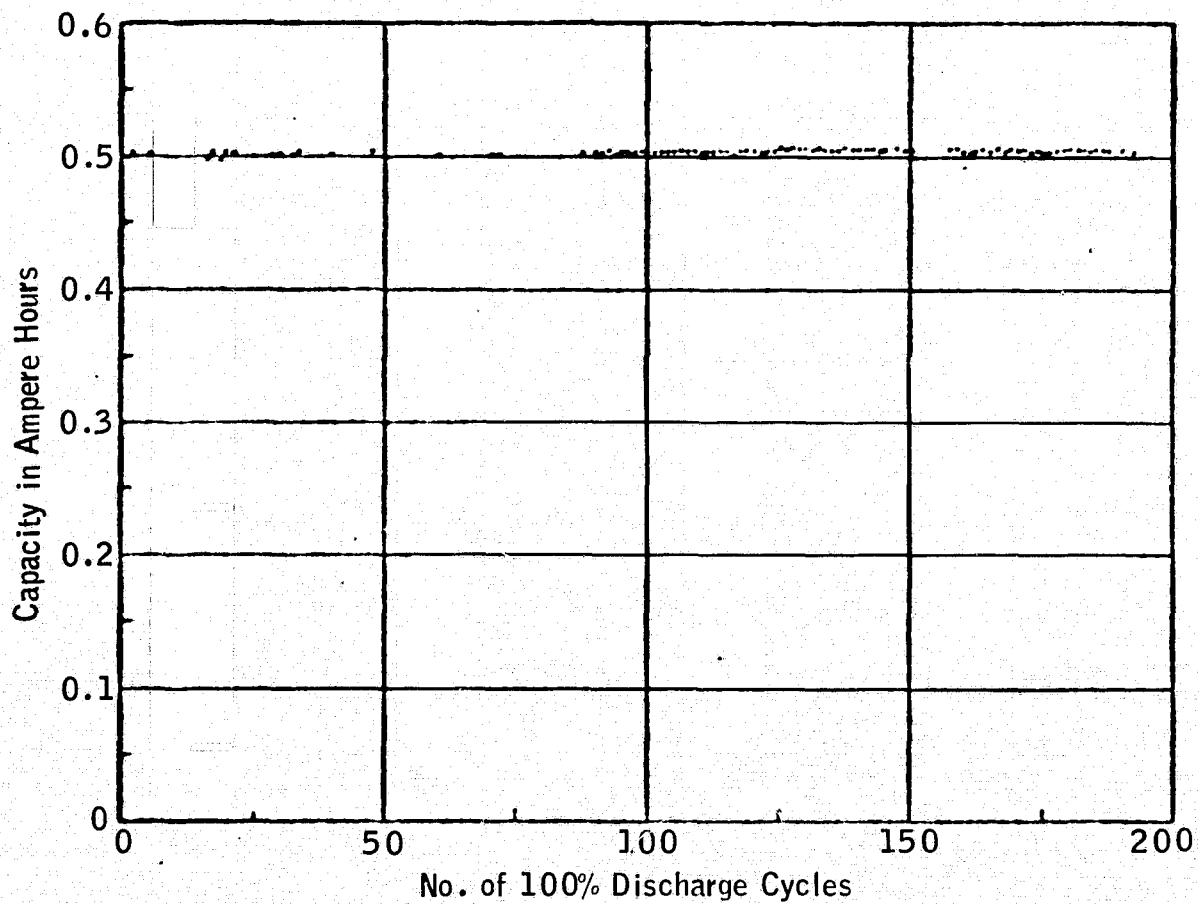
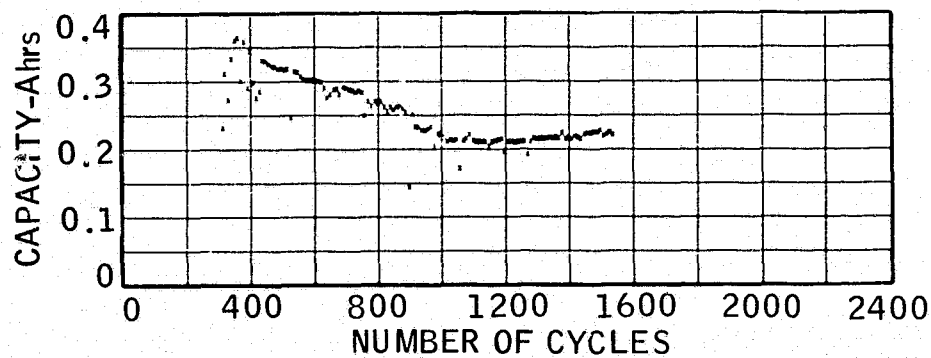


Figure 2-3: Life Cycling of Electrochemically Impregnated Nickel Electrodes

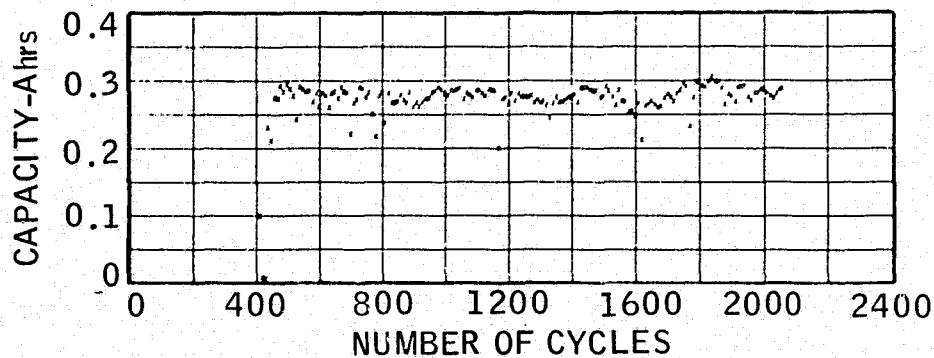
MacArthur (25) tested nickel electrodes made by McHenry's process, and compared them with vacuum impregnated electrodes of similar size and capacity. No differences in life cycling performance were seen between the two electrode loading methods. Results for electrochemically impregnated electrodes are given in Figure 2-4. The electrodes that had no overcharge showed no degradation whereas those with 75% overcharge showed an irreversible capacity loss. The reasons for this capacity loss are not understood.

Basis:

- o MacArthur, Ref. 25
- o C/2 charge
- o 10 minutes open circuit before discharge
- o C/2 discharge to 67% DOD
- o Sealed cells



a) 75% OVERCHARGE



b) NO OVERCHARGE

Figure 2-4: LIFE CYCLING OF ELECTROCHEMICALLY IMPREGNATED NICKEL ELECTRODES



### Takamura's Work

Takamura (4) did electrochemical impregnation of nickel electrodes at 20°C and found that to obtain high loadings there is an optimum amount of electricity (Figure 2-5), an optimum current density and nitrate concentration (Figure 2-6), and a dependence on temperature (Figure 2-7). Using 0.7 mm thick electrodes, he obtained capacities of 34 mAh/cm<sup>2</sup>. Takamura also reported the coulombic efficiency of the process (Figure 2-8), including in this determination the active material that sometimes formed on the exterior surface of the plaque, some of which even fell off. His work on the deposition mechanism showed that the principle reaction was the combination of nitrate ion with hydronium ion to form ammonia and water (equation 4). Thus his calculation of theoretical capacity is based on equation 4. Takamura obtained higher levels of impregnation of nickel electrodes than did McHenry (Figure 2-9), but his capacity during the first part of cycling was less stable (Figure 2-10). Cycling conditions were not reported.

### Beauchamp's Work

Beauchamp impregnated plaque under conditions close to those used by McHenry and got similar results, shown in Figure 2-11 for nickel electrodes and Figure 2-12 for cadmium electrodes. The maximum loading reached of 5.0 ampere-hours/ in<sup>3</sup> corresponds to approximately 1.25 g/cc of void for the nickel electrodes, and to approximately 1.0 g/cc of void for the cadmium electrodes.

Basis:

- o Takamura, Ref. 4
- o Curve A: 0.5 M  $\text{Ni}(\text{NO}_3)_2$ , 10  $\text{mA}/\text{cm}^2$
- o Curve B: 2.0 M  $\text{Ni}(\text{NO}_3)_2$ , 30  $\text{mA}/\text{cm}^2$
- o  $20^\circ\text{C}$

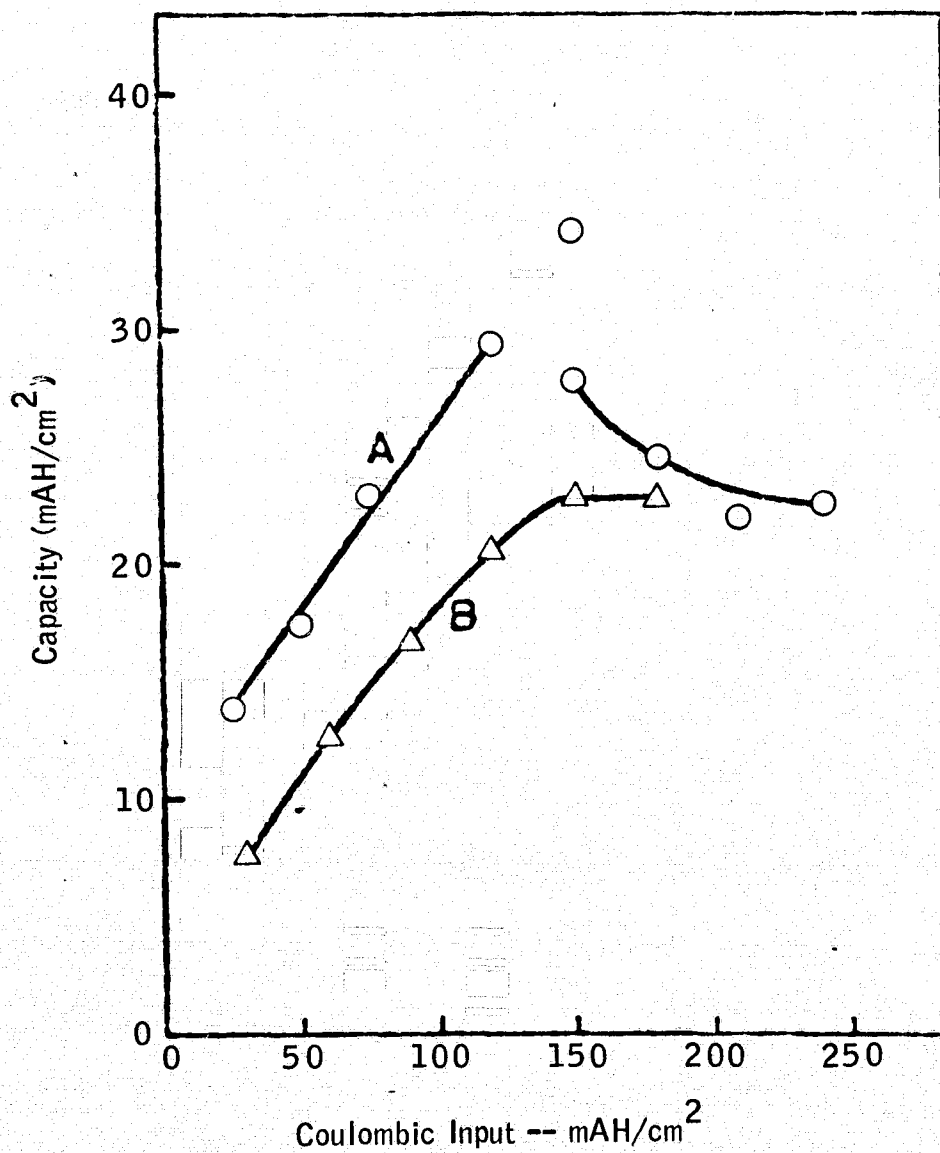


Figure 2-5: Effect of Coulombic Input on Capacity of Electrochemically Impregnated Nickel Electrodes

Basis:

- o Takamura, Ref. 4
- o Curve A: current density =  $10 \text{ mA/cm}^2$
- o Curve B: current density =  $30 \text{ mA/cm}^2$
- o Curve C: current density =  $60 \text{ mA/cm}^2$
- o  $20^\circ\text{C}$

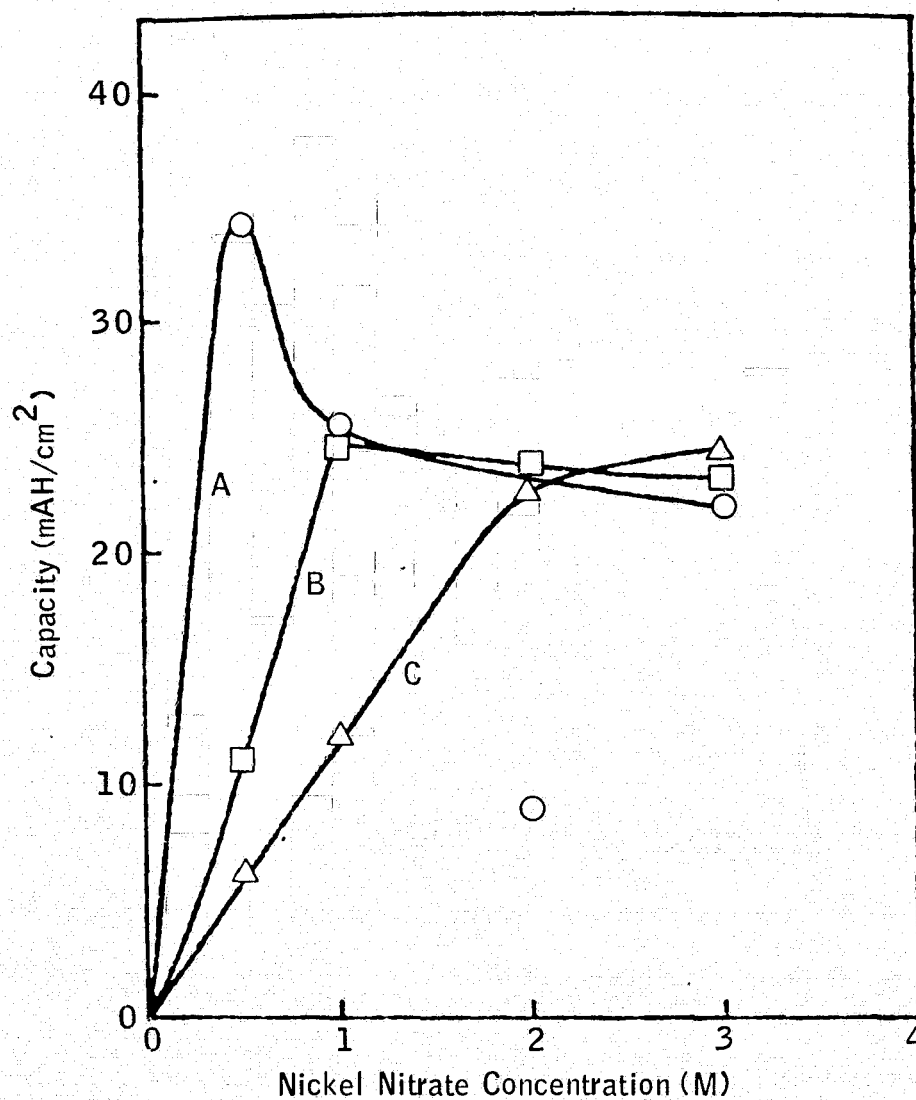


Figure 2-6: Effect of Nickel Nitrate Concentration on Capacity of Electrochemically Impregnated Nickel Electrodes

Basis:

o Takamura, Ref. 4

o Nickel Nitrate Molarity:

A = 0.5

B = 1.0

C = 2.0

D = 3.0

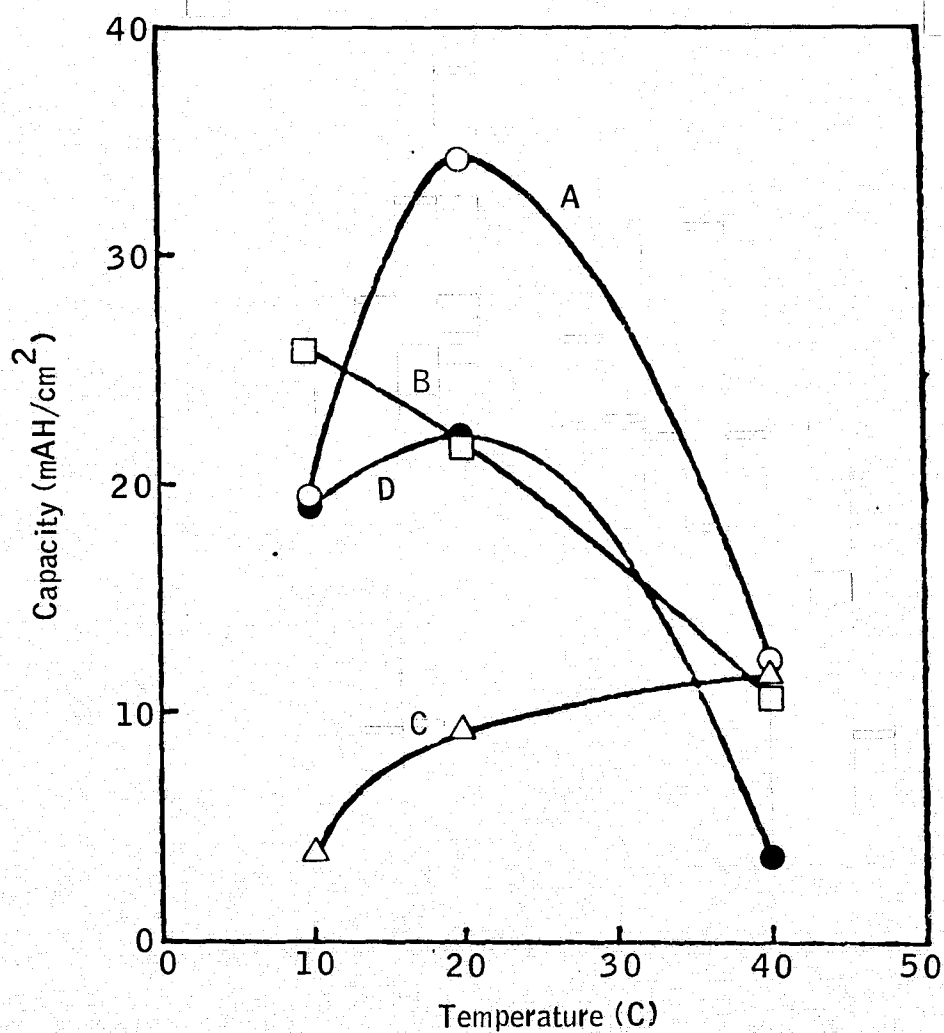


Figure 2-7: Effect of Solution Temperature on Capacity of Electrochemically Impregnated Nickel Electrodes

Basis:

- o Takamura, Ref. 4
- o 20°C
- o Nickel nitrate molarity:
  - A = 1.0
  - B = 2.0
  - C = 3.0

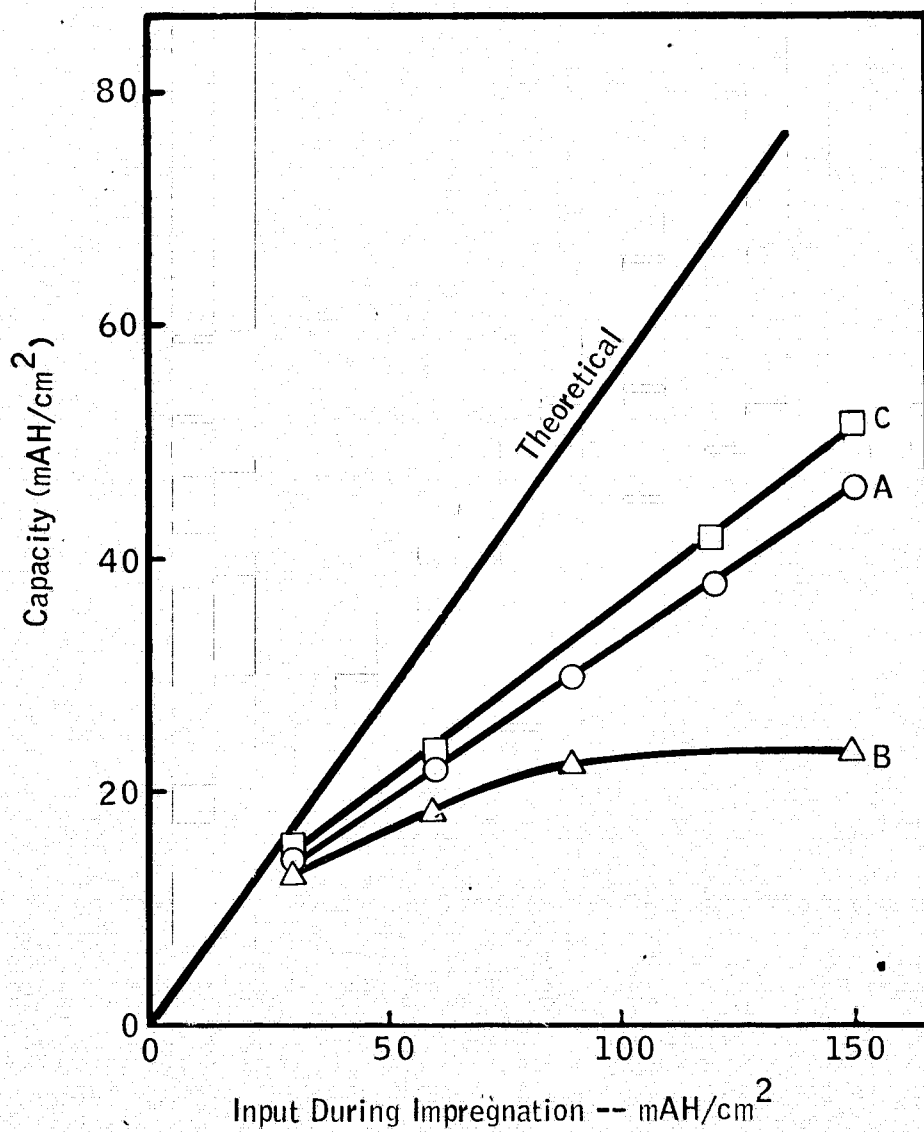


Figure 2-8: Coulombic Efficiency of Electrochemical Impregnation of the Nickel Electrode by Takamura

Basis:

- o Plate thickness =  $0.7 \pm 0.05$  mm
- o A = Takamura's data (Ref. 4)
- o B & C = McHenry's data (Ref. 23)
- o  $20^{\circ}\text{C}$

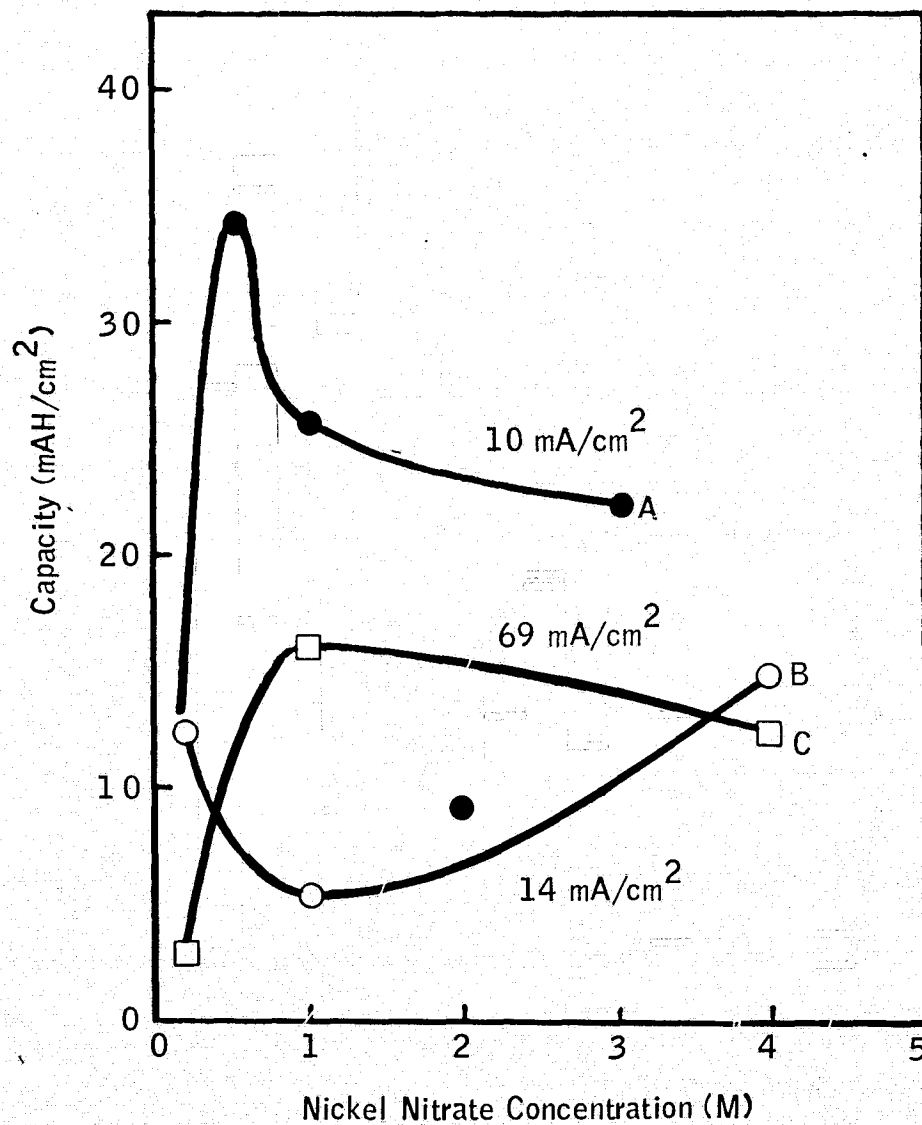


Figure 2-9: Comparison of Electrochemical Impregnation of the Nickel Electrode by Takamura and McHenry

Basis:

- o Takamura, Ref. 4
- o 20°C

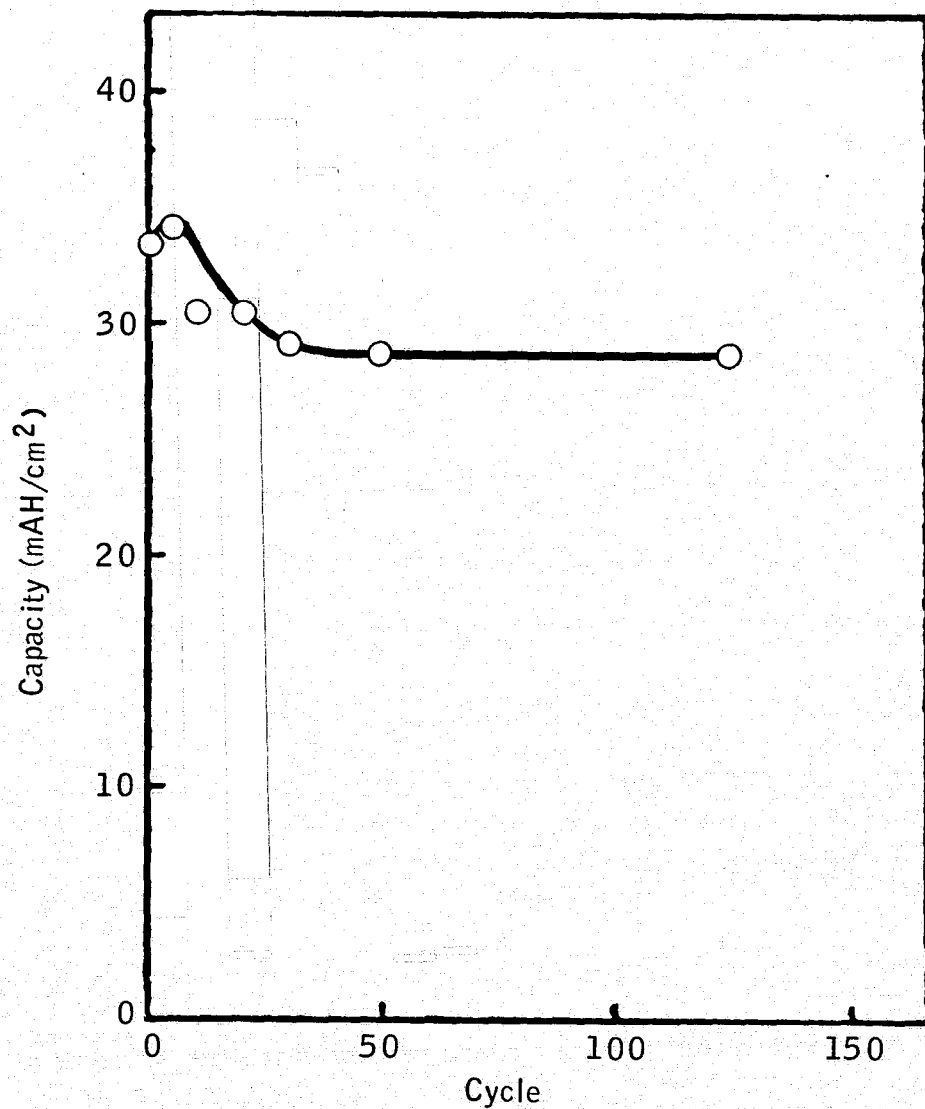


Figure 2-10: Capacity Stability During Cycling of Nickel Electrodes Electrochemically Impregnated by Takamura

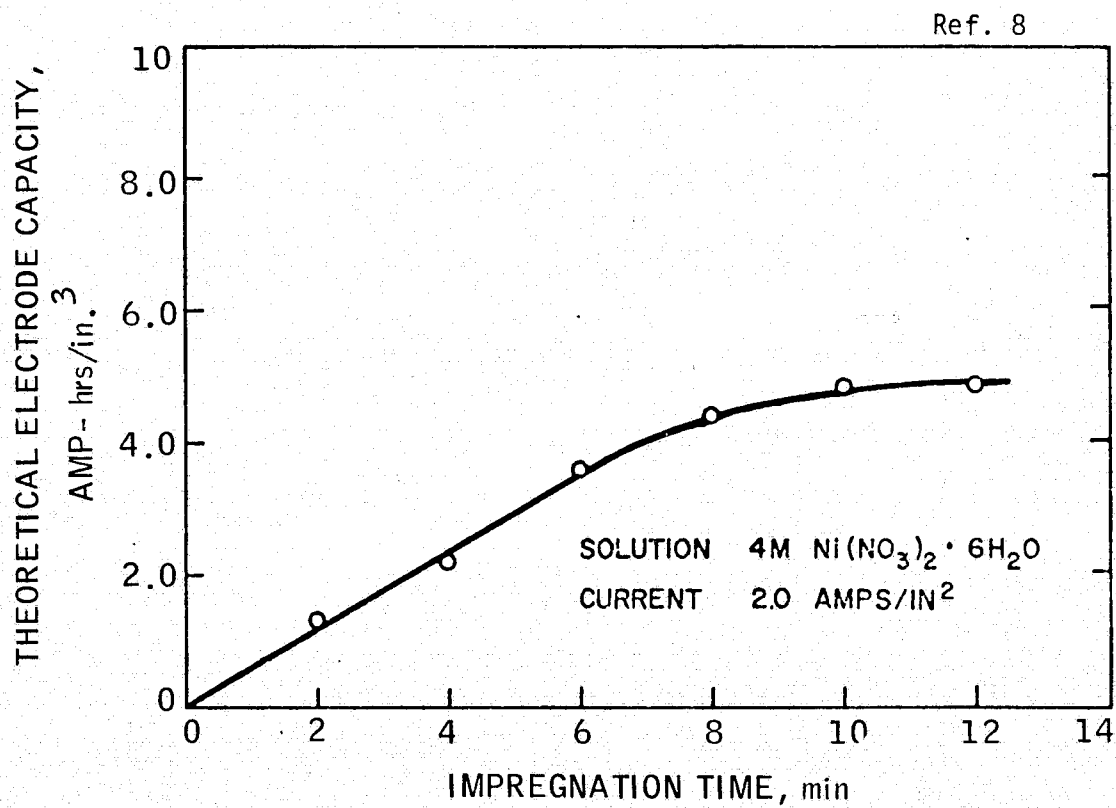


Figure 2-11: ELECTROCHEMICAL IMPREGNATION  
OF NICKEL ELECTRODES BY  
BEAUCHAMP -- 25°C



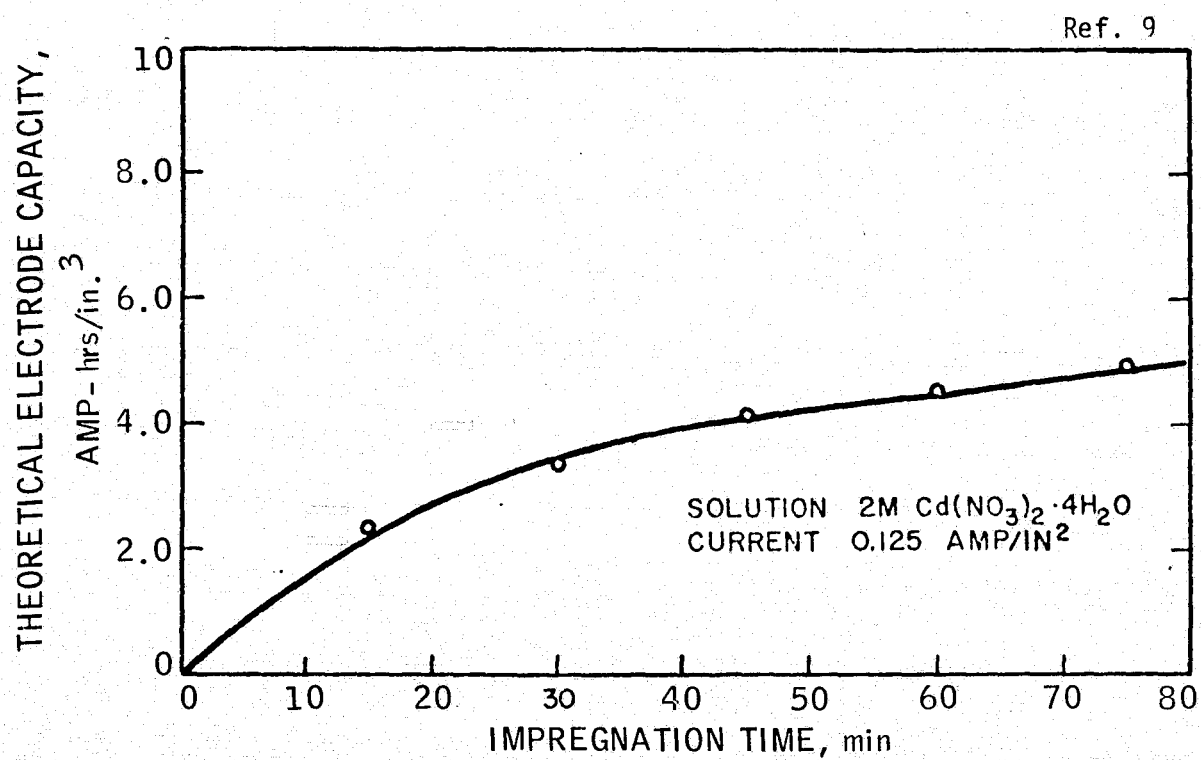


Figure 2-12: ELECTROCHEMICAL IMPREGNATION  
OF CADMIUM ELECTRODES BY  
BEAUCHAMP -- 25°C

Whereas McHenry had found no strong temperature effect during electrochemical impregnation over the range of  $25^{\circ}\text{C}$  to  $70^{\circ}\text{C}$ , Beauchamp (8 to 12) found that above  $75^{\circ}\text{C}$  a large increase in loading is possible. For the cadmium electrode, this is due to the much smaller crystals which form, probably because of a higher nucleation rate and crystal size reduction through dissolution. Electrochemical impregnation at  $105^{\circ}\text{C}$  produced large improvements. This is shown in Figure 2-13 for nickel electrodes and Figure 2-14 for cadmium electrodes, expressed as theoretical capacity; the relationship between actual capacity and weight gain should show trends similar to Figure 2-2. Beauchamp also found that the optimum loading at this temperature was not overly sensitive to solution concentration and current density (Figure 2-15).

A unique feature of Beauchamp's electrochemical impregnation method is the addition of sodium nitrite ( $\text{NaNO}_2$ ) to stabilize solution pH during impregnation (Figure 2-16), with buffering action occurring per reaction (11). Without a buffer, the solution would become more acidic as impregnation progresses. Using this buffer and 76 percent porous plaques 0.028 inches thick, highest loadings occurred with a current density of  $0.5 \text{ amperes/in}^2$  and a 2M solution of  $\text{Cd}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  or  $\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ . The maximum loading for both cadmium and nickel electrodes was 2.1 grams of active material per cc of void volume. This was attained in 60 minutes for the cadmium electrode and is equivalent to a loading density of  $9.7 \text{ ampere hours/in}^3$ . Maximum loading of the nickel electrode was reached in 75 minutes and corresponds to a loading density of  $8.5 \text{ ampere-hours/in}^3$ .

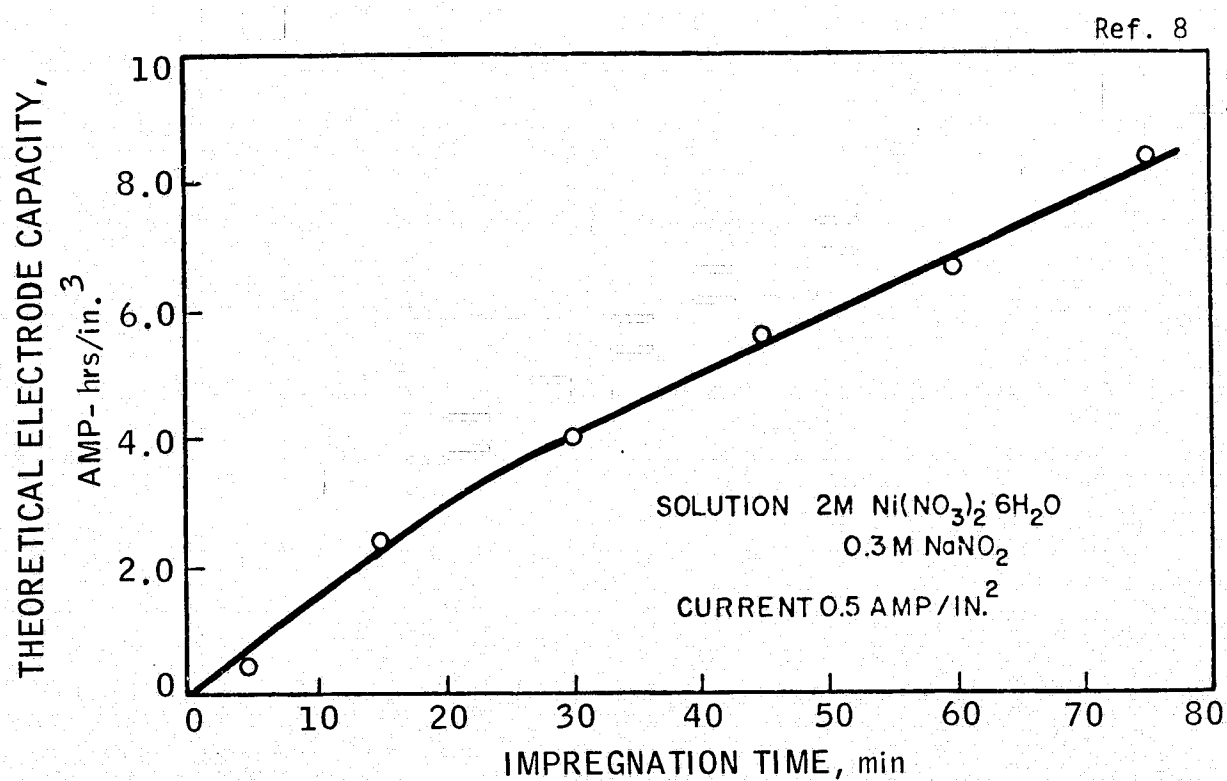


Figure 2-13: ELECTROCHEMICAL IMPREGNATION  
OF NICKEL ELECTRODES BY  
BEAUCHAMP -- 105°C

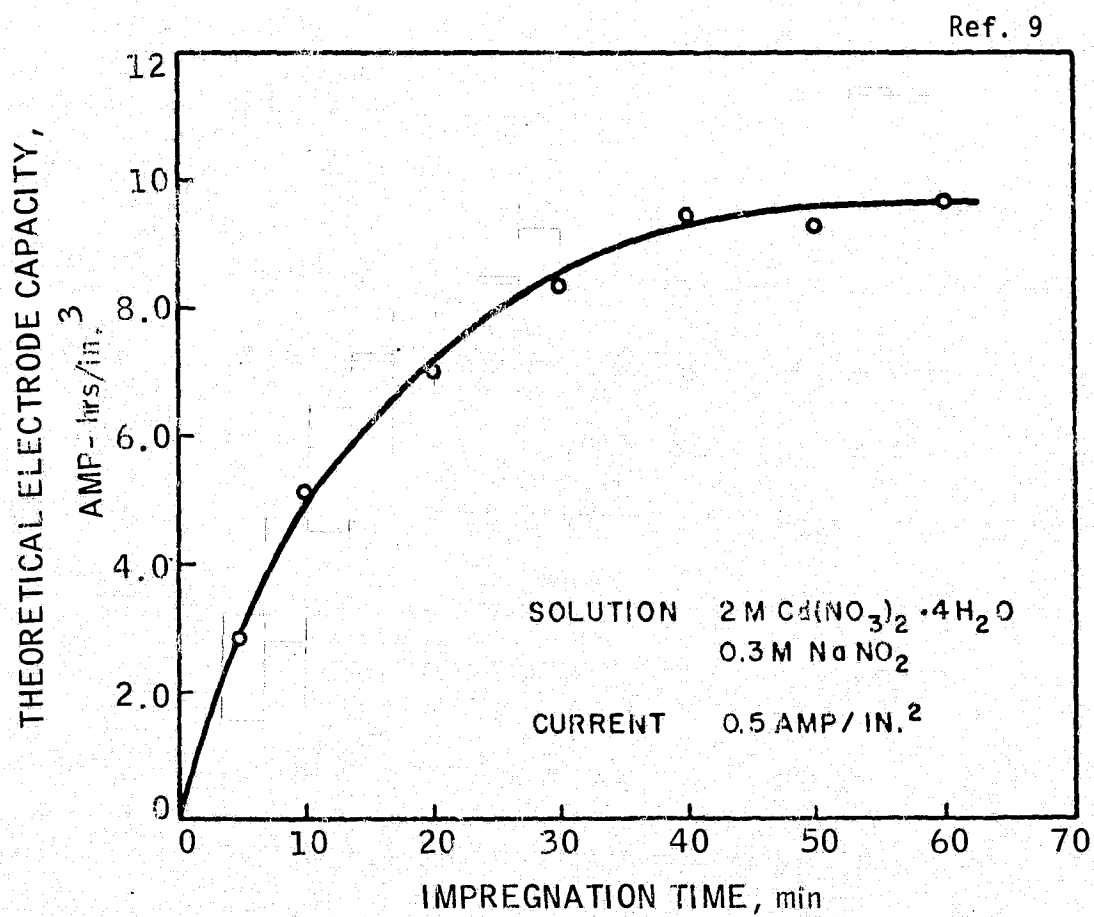


Figure 2-14: ELECTROCHEMICAL IMPREGNATION  
OF CADMIUM ELECTRODES BY  
BEAUCHAMP - - 104°C

Ref. 9

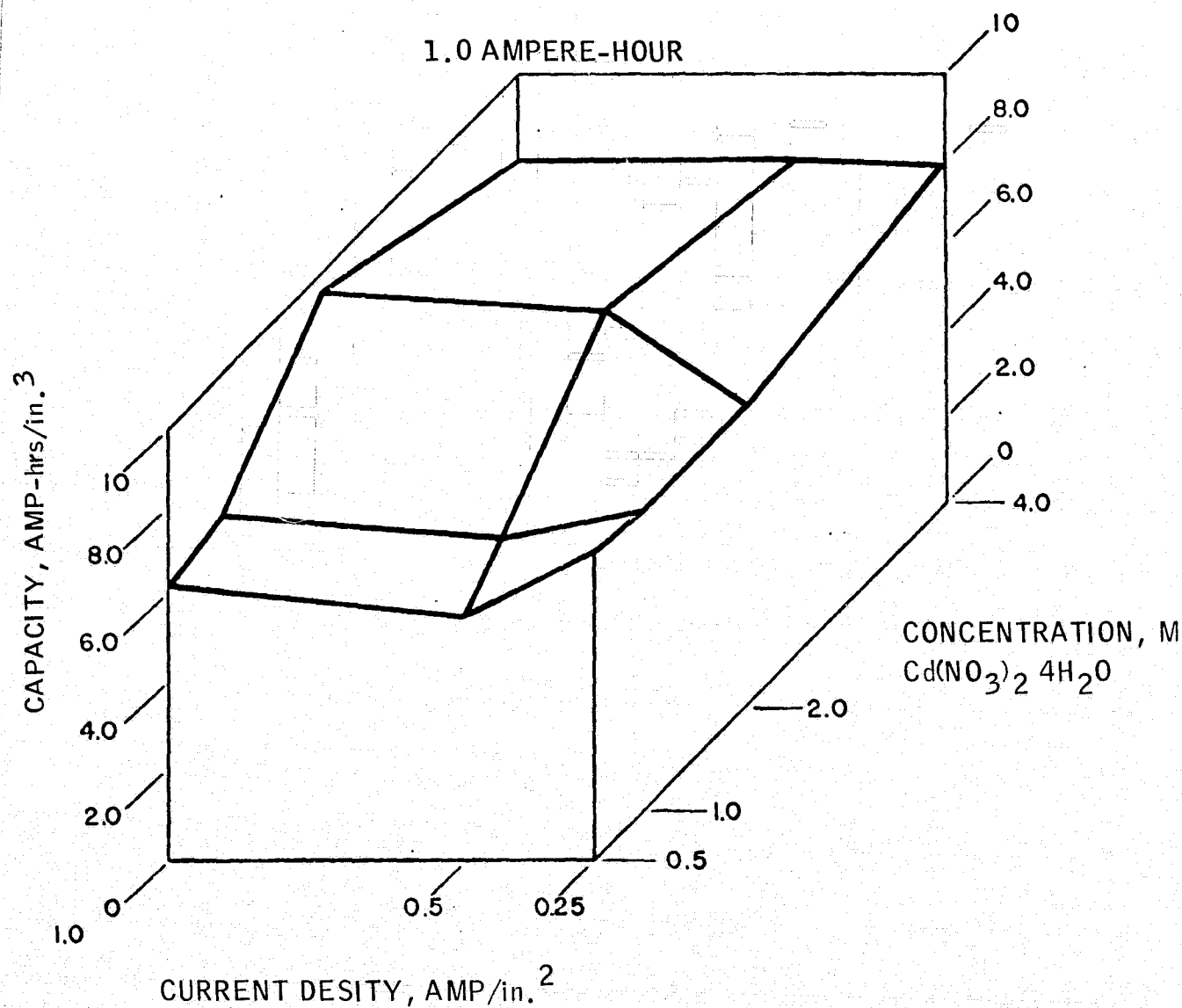


Figure 2-15: EFFECT OF CURRENT DENSITY AND SOLUTION CONCENTRATION ON ELECTROCHEMICAL IMPREGNATION OF CADMIUM ELECTRODES BY BEAUCHAMP -- 104°C

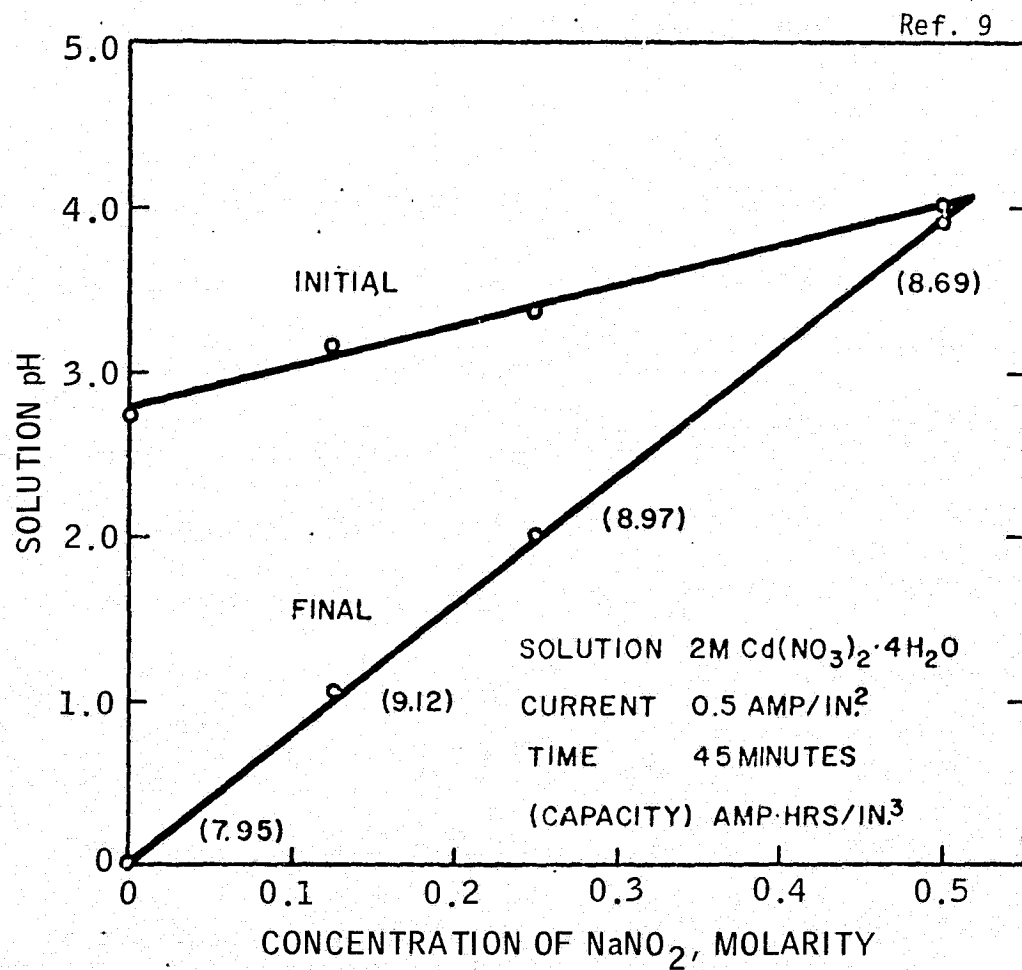


Figure 2-16: BUFFERING OF CADMIUM SOLUTION  
ACIDITY WITH SODIUM NITRITE ADDITIVE

Cycling test results of Beauchamp's electrochemically impregnated cadmium electrodes is given in Figure 2-17, based on data from Ref. 9. Such electrodes have greater efficiency than conventional ones, and are more constant. The plaques and loading levels differed on each of the three kinds of electrodes shown in Figure 2-17, however, factors other than impregnation method could have contributed to the observed performance differences. The improvement observed is significant, nevertheless, for high efficiency and stability of the cadmium electrode has been an elusive objective of much research.

The performance of nickel electrodes made by Beauchamp's high temperature process is shown in Figure 2-18. The tests were conducted with flooded electrodes, and for comparison were repeated on a comparable commercial electrode prepared by immersion techniques. The electrochemically prepared electrodes are seen to have better utilization, especially at high rates. Performance of sealed cells (Figure 2-19) is similar to that of flooded nickel electrodes (Figure 2-18) since the cells are positive limited.

The fact that the electrodes produced more than 100 percent of theoretical capacity, based on a one electron transfer, may be due to nickel oxides of higher valency produced at high charge rates. Corrosion did not seem to be responsible for the additional capacity, for subsequent tests showed that a loss in plaque weight of only 2 percent occurred after the active material was removed by dissolution. Capacities indicative of more than one electron transfer have been observed often with electrochemical impregnation. The fundamental reason for this is not known. Research appears to be worthwhile both to determine if further gains can be made, and to provide this capacity

Basis:

- o Charge C/2 for 4 hours (5 hours for aerospace electrodes)
- o Discharge C/2 to 1.0 volt
- o Commercial and Bell Telephone Labs Electrodes -- Ref. 8
- o Aerospace Electrodes -- Boeing Spacecraft Cells

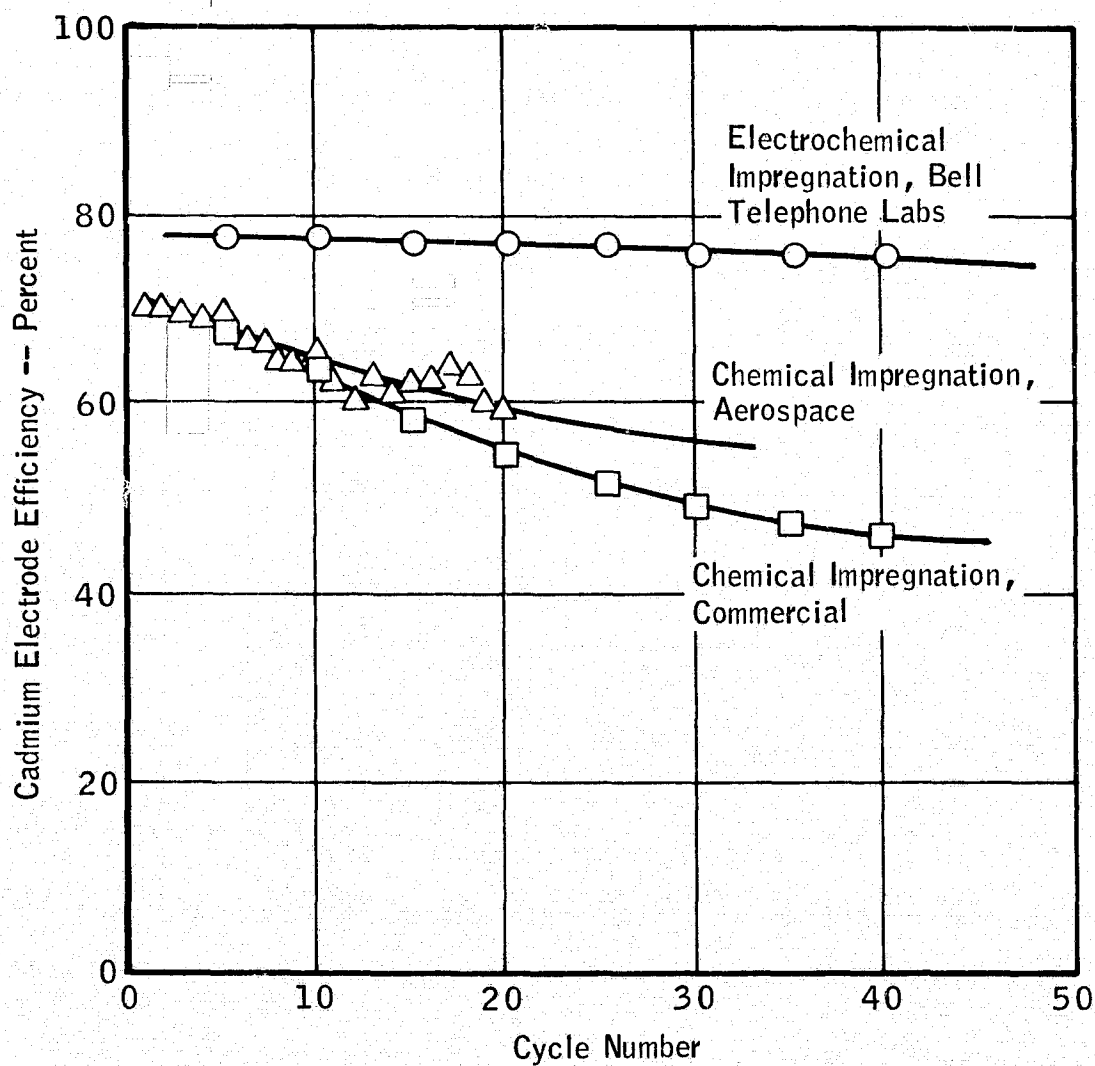


Figure 2-17: Cycling Degradation of Cadmium Electrodes



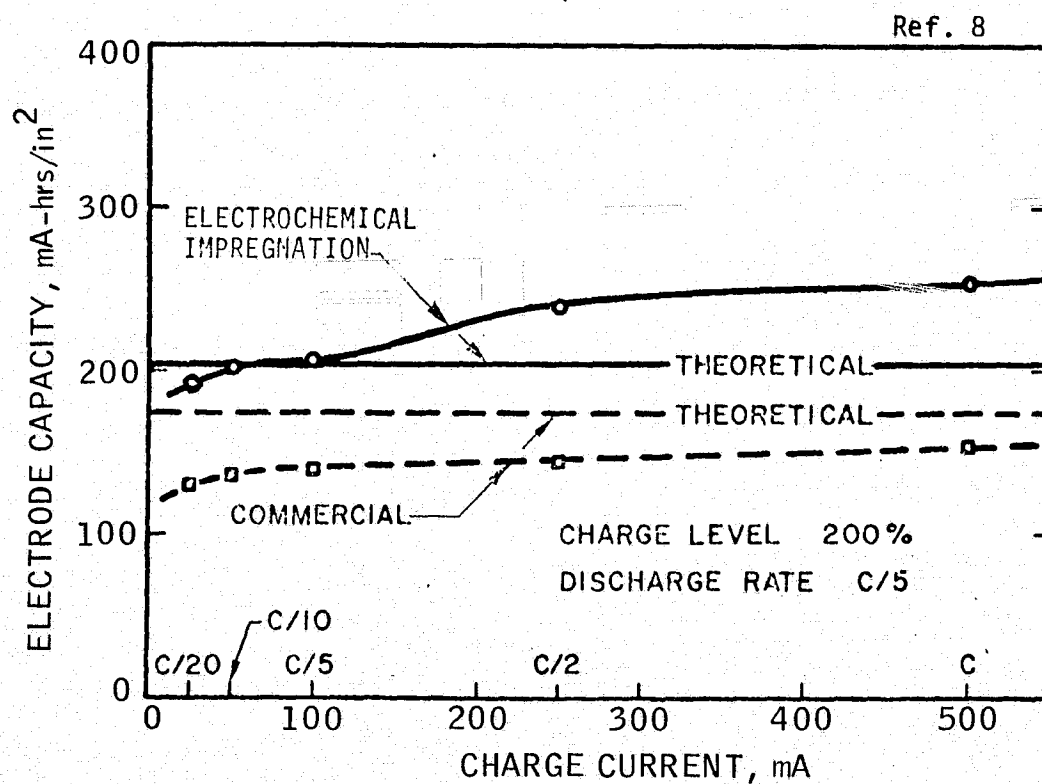


Figure 2-18: CAPACITY DURING CYCLING OF FLOODED NICKEL ELECTRODES

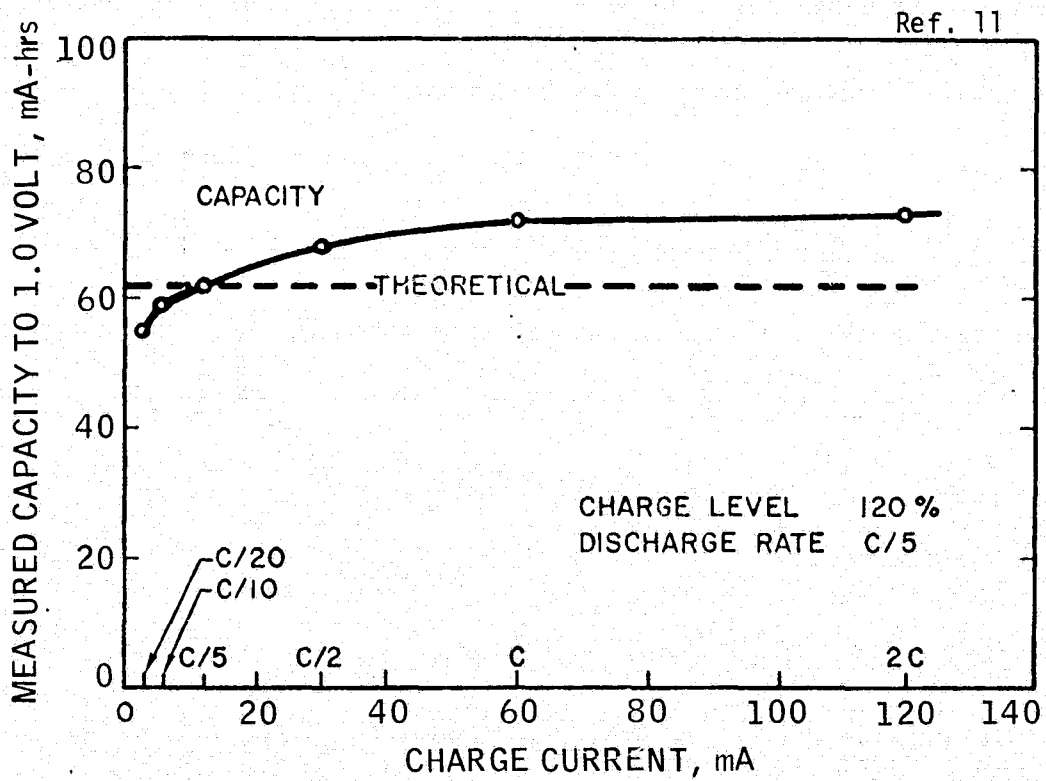


Figure 2-19: PERFORMANCE OF ELECTROCHEMICALLY IMPREGNATED NICKEL CADMIUM CELLS

improvement at lower charge rates. It is only rarely that aerospace batteries are charged faster than C/2, which would be necessary to take advantage of such capacity improvements. The fact that charging at high rates produces different effects than low rates raises further questions on the validity of conducting accelerated tests by speeding up the charge rate.

The cycling performance of nickel electrodes under stressed conditions with deep discharges is given in Figure 2-20 for flooded electrodes. Capacity increases with cycles and then appears to stabilize. Cycling behavior of sealed cells (Figure 2-21) is similar to that of flooded nickel electrodes. The fact that capacity initially increased with cycling appears unrelated to the charge rate, since it increased both at 2C charge with flooded nickel electrodes and at C/10 with sealed cells. Such a capacity increase with cycling presents a number of problems, such as cell capacity matching and maintenance of the desired negative-positive ratio. In order to properly set precharge, it is important to know whether this capacity increase is initially in the cell in the charged or discharged state.

#### Kroger's Work

Kroger experimented with some modifications to the chemical impregnation process to obtain electrochemically impregnated nickel electrodes. This process was called the modified constant potential electro-deposition process (26). Plaque with nickel screen substrate was used, and the process employed nickel counter electrodes. Solution temperature was relatively low, in the range of 34 to 40°C. Utilization averaged approximately 90% for 20 Ah cell electrodes, and 84% for 50 Ah cell electrodes. By compressing electrodes from 0.064 cm to 0.052 cm it was possible to obtain an initial specific capacity of 7.5 Ah/in<sup>3</sup>.

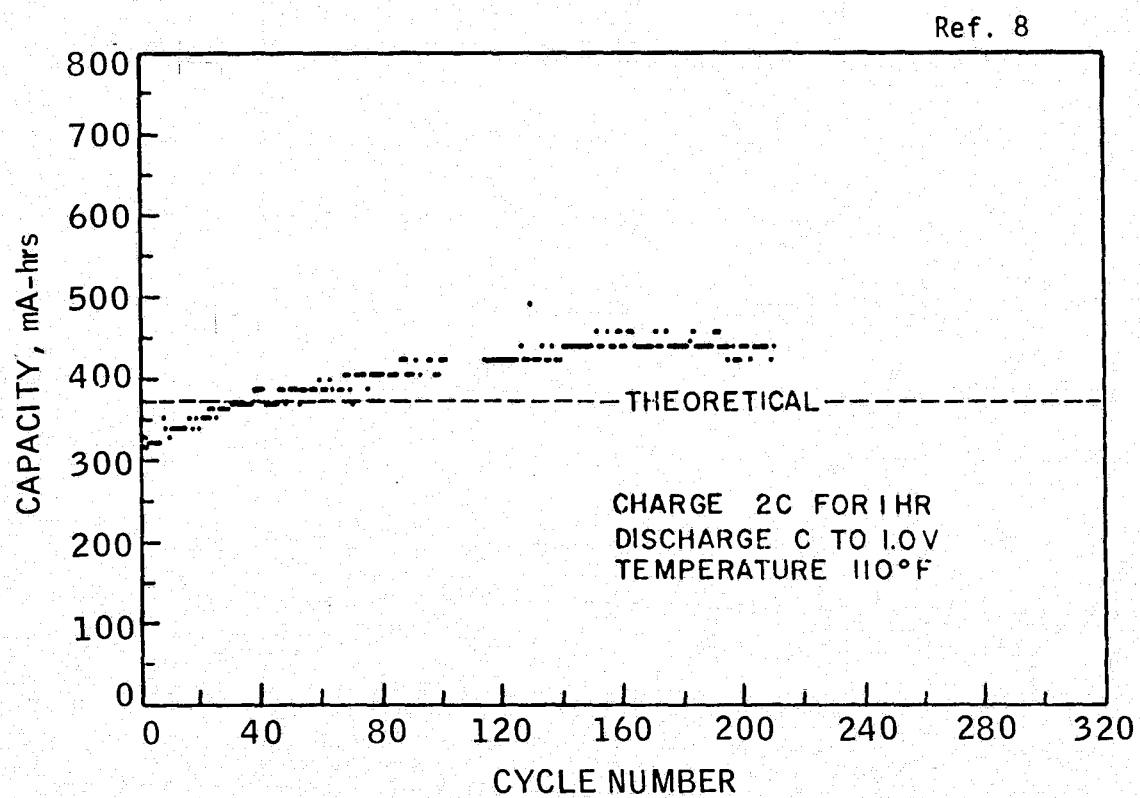


Figure 2-20: STRESSED CYCLING OF FLOODED NICKEL ELECTRODES

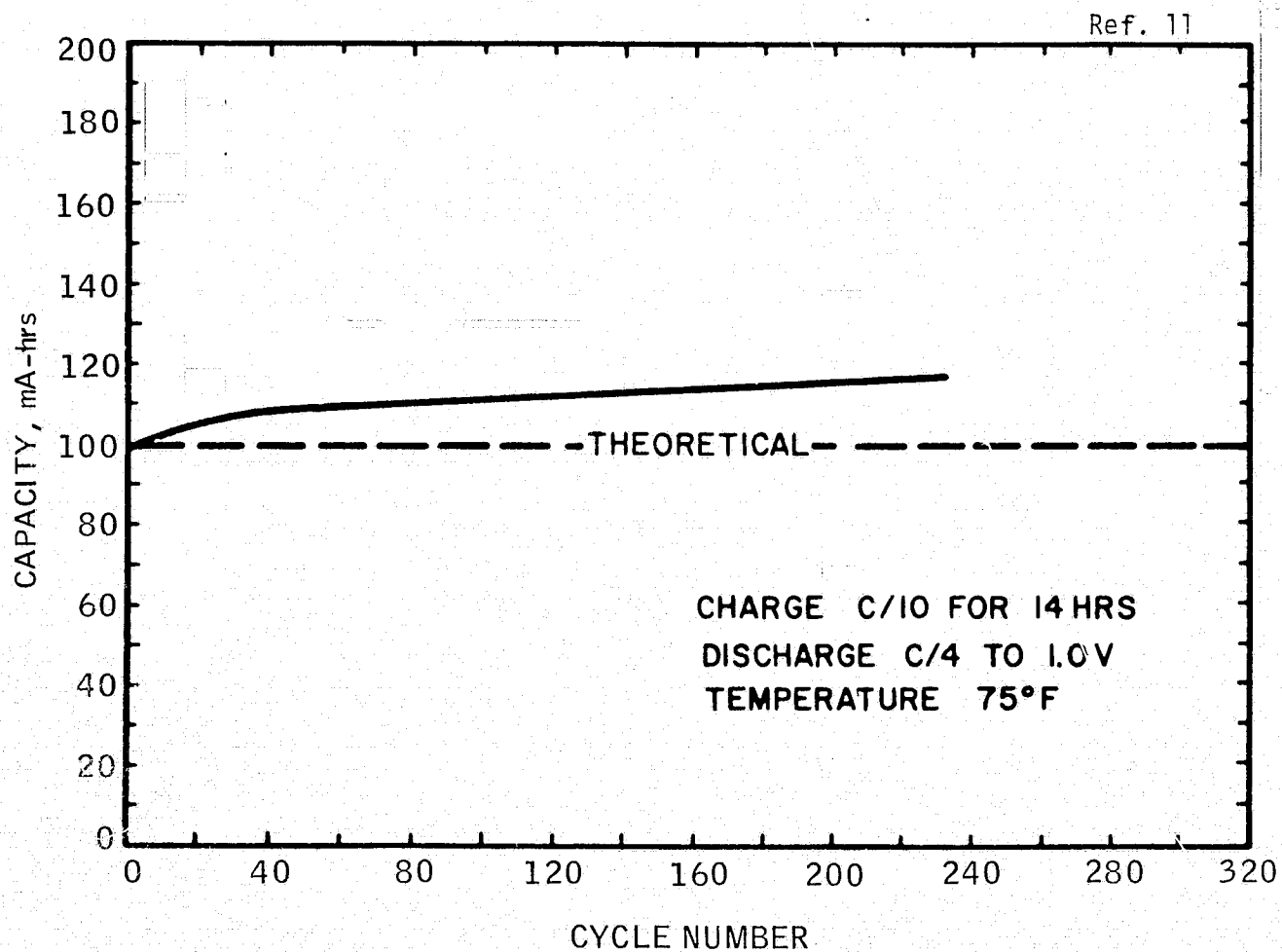


Figure 2-21: CAPACITY CYCLING OF ELECTROCHEMICALLY IMPREGNATED NICKEL CADMIUM CELLS

This process apparently is unable to maintain steady state diffusion rates that are adequate to fully impregnate electrodes. As a result, the impregnation is carried out in four steps of about a half hour each. Corrosion would be expected during impregnation in such a method. However, the most significant amounts of corrosion occurred in the course of 4200 repetitive cycles. This could be detected only by chemical analysis, for it was not apparent by observation. Typically, 12 percent of the nickel metal was lost by corrosion. The electrodes were compressed during manufacture from 0.064 cm to 0.052 cm, but after only seven cycles they grew to 0.0606 cm, increasing to 0.0652 cm after 648 cycles and to 0.0793 cm after 4273 cycles. Such dramatic thickening is not typical of the electrochemical impregnation method.

It appears that this process is a combination of electrochemical conversion and electrochemical impregnation. This did not produce satisfactory electrodes, for they corroded, became swollen, and exhibited memory effects. Analysis showed that oxidation states greater than  $3^+$  occurred in new cells but was not present in cycled cells. A large amount (up to 45%) of uncharged active material was present at the end of charge, and an appreciable amount (up to 20%) of charged active material was present at the end of discharge. Also, compaction appears to be undesirable not only because the plates swell back again after cycling, but also because compaction produces pores with narrow openings (3), which are the worst kind because diffusion is impaired and the openings can become plugged easily.

### Holleck's Work

Holleck (27,28) tested the effect of manufacturing variables in a factorial design experiment in which the following variables were examined:

A -- Plaque type at three levels

$A_0$  -- dry sinter

$A_1$  -- slurry based, Ni screen substrate

$A_2$  -- slurry based, perforated sheet substrate

B -- Plaque thickness at two levels

$B_0$  -- thin (20 mils objective)

$B_1$  -- thick (30 mils objective)

C -- Impregnation method at three levels

$C_0$  -- chemical conversion

$C_1$  -- vacuum impregnation, electrochemical conversion

$C_2$  -- electrochemical impregnation ( $104^{\circ}\text{C}$ , pH 4,  $\text{NaNO}_3$  added;  
Ni @  $0.5 \text{ A/in}^2$ , Cd @  $0.25 \text{ A/in}^2$ )

D -- Loading amount at two levels

$D_0$  -- Low loading ( $5 \text{ Ahr/in}^3$ )

$D_1$  -- High loading ( $8 \text{ Ahr/in}^3$ )

The plates were then tested in flooded conditions against oversized counter electrodes. The cycling test simulated a near-Earth orbit with 30 minutes discharge to 25% DOD, and 60 minutes charge including 8% overcharge. Discharge of the negatives started with from 80% of full charge, whereas discharge of the positives started from full charge. Cycling was carried out at room temperature for 100 cycles.

Results from this work are difficult to interpret because the plaque loading methods, especially the electrochemical impregnation method, was not optimized before making the comparative tests. Nickel electrodes, for example, had surface buildup of active material. Also, during the cycling tests there was not enough overcharge to keep the electrodes in a full state of charge. Nevertheless, the following useful conclusions could be drawn from these tests.

- 1) The electrochemical impregnation method is much more sensitive to the plaque structure than the other methods, and is affected by the largest number of variables, especially with the cadmium electrode. This is understandable, since electrochemical impregnation depends on a balance of diffusion processes.
- 2) For electrochemical impregnation, low loadings were best with thin plaques, and high loadings were best with thick plaques.
- 3) Cadmium electrodes with low loadings degraded less with cycling, irrespective of the method of loading.
- 4) Cadmium electrodes made by the electrochemical impregnation process were less affected by cycling than those made by other methods. This is believed to be the result of a better distribution of active materials in the plaque structure. These electrodes also gave the smallest polarization.
- 5) Weakening of the plaque structure by corrosion is less with electrochemical impregnation than with the other impregnation methods.



### Rubin and Turchan's Work

Rubin and Turchan (29) developed high temperature electrochemical impregnation processes for both nickel and cadmium electrodes, based on the method of Beauchamp (8 to 12). Their objective in this work was to design a high energy density cell of aerospace quality. They found that success with this process was critically dependent on the physical characteristics of the porous nickel plaque. Detailed parametric studies were made of process variables, including current density, nickel or cadmium nitrate concentration, sodium nitrite concentration and solution pH. Based on laboratory scale tests, the best operating conditions found are shown in Table 2-2. Counter electrodes used were platinized titanium.

Even though the nickel plaque has cathodic protection from corrosion during impregnation of the cadmium electrodes, it was found that some corrosion does occur. To prevent this, the plaques were lightly oxidized by heating in air prior to impregnation. Side effects of this were (1) buildup of active material on the outside of the plaque was minimized; (2) utilization of the negative plate active material was reduced to 80% of theoretical; and (3) increase in plate thickness during impregnation was much reduced. Sodium nitrite used in the solution maintained pH control, and was found also to be necessary in preventing corrosion of the nickel sinter, even with a prior light oxidation of the sinter. The improvements experienced in weight gain due to the use of passivation by nickel oxide are shown in Figure 2-22.

Typical nickel positive electrodes made in this work had a sinter porosity of 83% (considering the substrate, the apparent porosity was 79%), a thickness of 0.029 inches, a flooded capacity of  $0.20 \text{ Ahr/in}^2$ , and an efficiency of

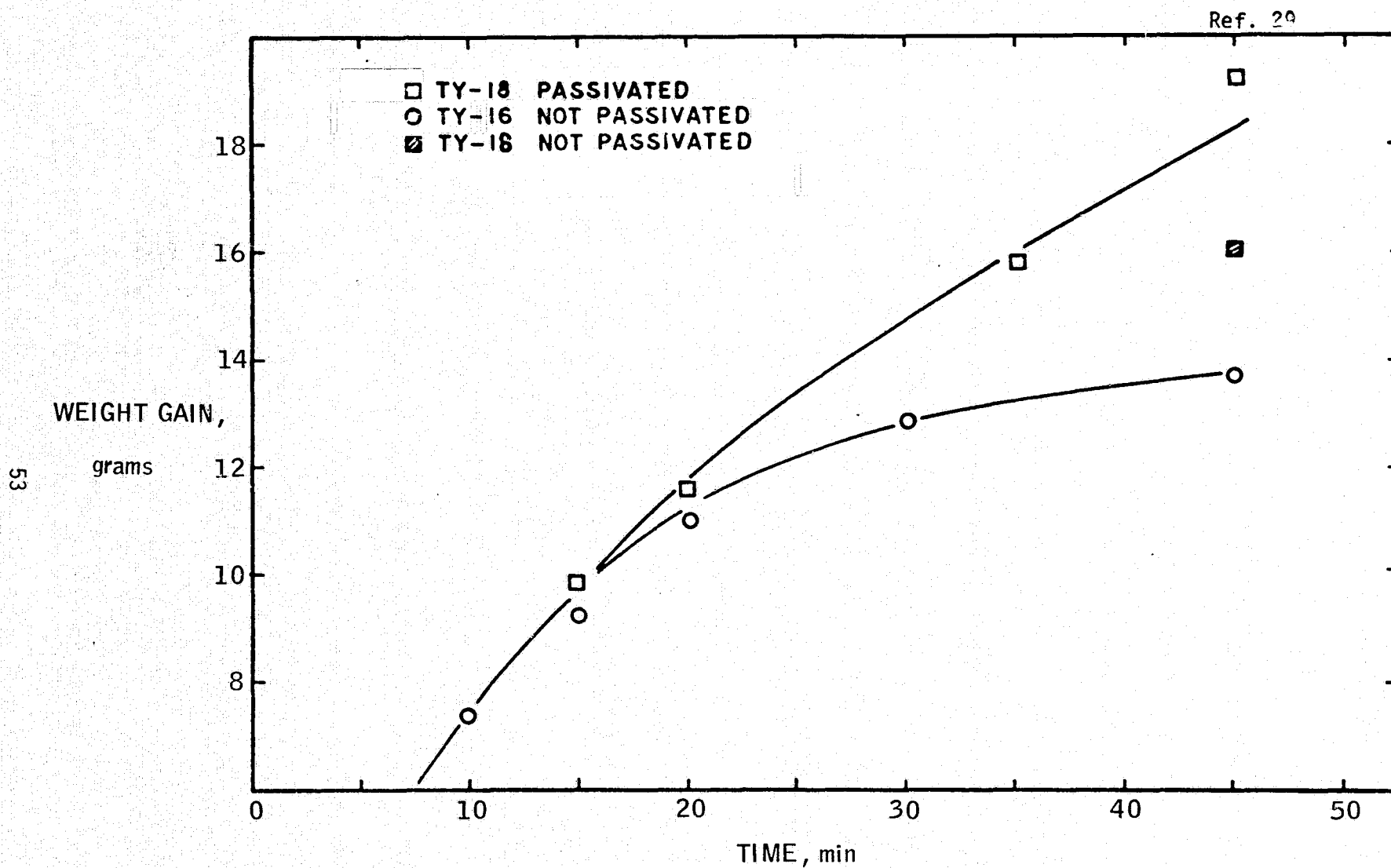


Figure 2-22: EFFECT OF NICKEL SUBSTRATE PASSIVATION ON  
ELECTROCHEMICAL IMPREGNATION OF CADMIUM  
ELECTRODES

125%, based on a one electron transfer. Typical cadmium negative electrodes had a sinter porosity of 83% and a thickness of 0.030 inches, a flooded capacity of 0.257 Ahr/in<sup>2</sup>, and an efficiency of 77%. Development of the cadmium electrode posed some problems that were not fully resolved. One was the non-uniform distribution of active material within the plaque structure, with some deposition of active materials on the plate surface. This was due in part to the accumulation of nitrate ion in the bath during continuous impregnation. Another problem was that the cadmium electrode efficiency was in some cases lower than it should have been, due to insufficient development time to obtain the sinter porosity as high as was desired.

TABLE 2-2 : RUBIN AND TURCHAN'S CONDITIONS FOR ELECTROCHEMICAL IMPREGNATION OF NICKEL AND CADMIUM ELECTRODES

	Nickel Electrode	Cadmium Electrode
Ni(NO <sub>3</sub> ) <sub>2</sub>	2.0 M	--
Co(NO <sub>3</sub> ) <sub>2</sub>	0.1 M	--
Cd(NO <sub>3</sub> ) <sub>2</sub>	--	2.0 to 3.0 M
NaNO <sub>2</sub>	0.3 M	0.3 M
pH	4.0	2.0 to 3.0
Temperature	105°C	105°C
Current Density	0.5 A/in <sup>2</sup>	0.5 A/in <sup>2</sup>
Current duration	75 min	40 min

### Hardman's Work

This method of electrochemical impregnation (30) applies to nickel electrodes, and is unique in that the plaques are made of metallic bonded fibers.

Capacity is high for this type construction, reaching  $6.2 \text{ AH/in}^3$  on electrodes 0.075 in. thick. This process is an especially important one, for it has been reduced to practice at Westinghouse (31), being one of the few to have done so. Even so, the process is not fully optimized yet.

Experience with electrochemical impregnation has shown that the results are very sensitive to the plaque geometry. Plaque geometry is not defined in the Hardman patent, however, except to state that the individual fibers were 0.00046 to 0.00117 inches in diameter and 1/8 inch long, and that the plaque was 90 percent porous. Without more information on the plaque, the details of the impregnation process are not of great value and so are summarized only briefly here.

The process uses a consumable nickel anode, chosen at least in part because nickel is cheaper as a metal than as nickel nitrate\*. The aqueous electrolyte is 50 to 80 percent concentrated, consisting of 20 parts nickel nitrate hexahydrate, one part cobalt hexahydrate, and having a specific gravity of 1.5 to 1.6. The pH was between 0.5 to 1.1, presumably maintained by addition of nitric acid. The preferred current density is  $50 \text{ ma/cm}^2$  projected area, and results in the black nickel hydroxide.

\*Cadmium, on the other hand, is cheaper as the nitrate than as the metal.

There are a number of features of this process which are of special interest. One finding was that oven drying caused flaking and loss of active material, so drip drying in air was substituted. Another feature is that a large amount of nitrate is trapped in the nickel hydroxide precipitate, up to 20 percent by weight of the impregnated material (comparative data appears not to be available for other electrochemical impregnation processes). As a result of this large amount of nitrate remaining, a relatively large quantity of ammonia is produced during formation, necessitating special procedures. Since the fiber plaque is flexible, it is found that after formation the plaque has expanded, spreading the fibers apart and opening up the spongy mass.

Hardman's process appears to be unable to maintain steady state diffusion rates that are adequate to impregnate electrodes. As a result, impregnation is conducted in about six pulses of 20 minutes each with a five to ten minute rest between pulses. The rest periods give time for concentrations to readjust, but also expose the electrodes to the possibility of corrosion. In spite of this, corrosion does not appear to have been a problem. As with Kroger's work (26), this process appears to be a combination of electrochemical conversion and electrochemical impregnation.

The basic difficulty appears to be associated with the fact that nickel ions must react with  $\text{OH}^-$  ions that have been produced electrochemically. Apparently the nickel ion mobility is insufficient to maintain adequate impregnation rates. The  $\text{OH}^-$  ions, on the other hand, must be prevented from diffusion out of the pores too fast, which is part of the purpose of operating at low temperature. It would be of great interest to obtain more information on problems of this kind, for they are basic to the question of why electrochemical

impregnation processes do or do not work well. For example, it is important to know whether the ammonia fountain effect (5) actually occurs, and the relationship of nickel ion and hydroxyl ion diffusion to a variety of factors that they are sensitive to.

#### Seiger and Puglisi's Work - - HELIOTEK/SPECTROLAB

The electrochemical impregnation method used by Seiger, Puglisi and co-workers is based on Pickett's method, using, for nickel electrodes, an alcoholic/aqueous medium having a pH ranging from 1.5 to 2.5 and operated at 80°C. The impregnation solution (32) was made up of 1.8M  $\text{Ni}(\text{NO}_3)_2$  plus 0.2 M  $\text{Co}(\text{NO}_3)_2$ . The solvent consists of equal parts by volume of water and denatured ethyl alcohol, denatured (Government Formular C) with methyl alcohol, ethyl acetate, methyl isobutyl ketone, and nonleaded gasoline. Sufficient nitric acid was added to produce a pH of 1.5, although pH in such a solution has an imprecise meaning. Isopropyl alcohol in the denaturant causes the bath to deteriorate, probably from by-products of isopropyl alcohol reactions. The effects of other denaturants used in the selected formula are not known, though no problems have been identified from their use.

Impregnation of cadmium electrodes was accomplished with a 2.0 M cadmium nitrate solution in alcoholic/aqueous medium of pH 3.5. Pure cadmium counter electrodes were used, being sacrificed during impregnation. Constant current was found to be acceptable for impregnating cadmium electrodes, but an alternating current pulse asymmetric with respect to time was found to be best for highly loaded plates (17,32). With plaques ranging from 75 to 82 percent porosity, the greatest loadings were obtained with 82 percent porous plaque.

The efforts of Seiger, Puglisi and coworkers to quantize the relationships between utilization, sinter porosity and loading are important steps to obtaining optimum designs (33,34). Equivalent data appears not to exist in the literature for more conventional methods of impregnation. Though these findings appear to be generally valid, utilization is not a well understood subject, and more data are needed before we can be certain that a general correlation has been established. For example, it is known that under some conditions efficiency increases with loading level, whereas under other conditions it decreases with loading level. Even assuming the data of Seiger and Puglisi to be typical, there are additional analyses that would be useful to establish the optimum electrode design for use in a cell, since the minimum volume and minimum weight positive electrodes differ in design. It should be noted that most of the work of Seiger and Puglisi on the nickel electrode was done with the addition of nine percent cobalt hydroxide, which is somewhat higher than commercial practice.

The plaque used for electrochemical impregnation has a major influence on the resultant electrode. Seiger and coworkers (33) investigated the physical and chemical interactions. One important finding was that utilization of nickel electrodes is dependent primarily on sinter porosity (Figure 2-23).

Impregnation methods used for these data were molten salt, aqueous solutions, and electrochemical. Thus, the dependence of nickel electrode utilization on porosity would appear not to be uniquely an attribute of the impregnation method. Perhaps the high utilization reported by Beauchamp and others was due to this effect, rather than to the electrochemical impregnation method per se. Using these data, Seiger calculated (33) that the optimum capacity per unit volume for the nickel electrode occurred at a plaque porosity of 77 percent.

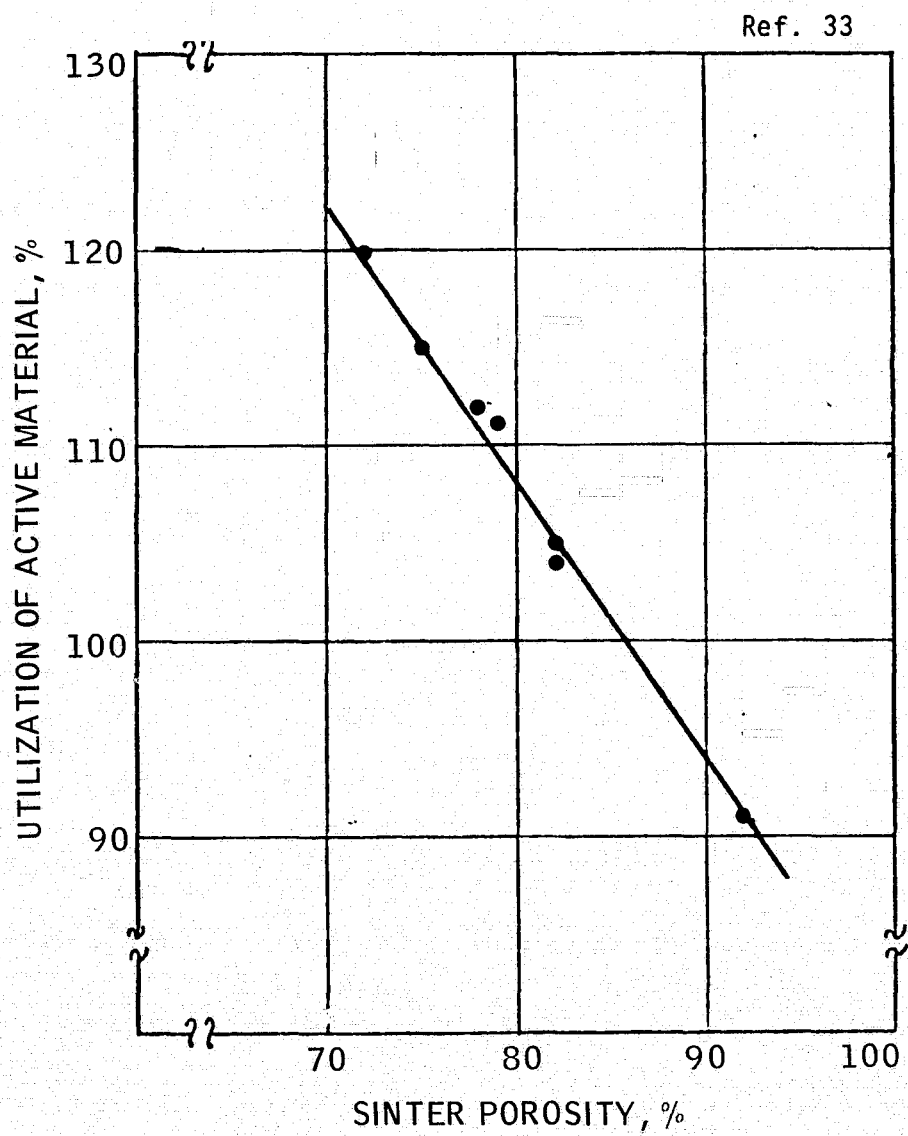


Figure 2-23: Effect of Sinter Porosity on Utilization of Nickel Electrodes



This has since been verified experimentally in work at Yardney. The maximum capacity per unit weight, however, is calculated (33) to be greatest as the sinter porosity approaches 100 percent and has been verified experimentally at Yardney. However, as the plaque is made more porous, strength becomes of greater importance, and the tendency to blister and shed increases. The practical upper limit was considered to be 84% porosity using plaques 36 mils thick.

In agreement with other workers, Seiger found that a number of cycles are required for nickel electrodes to develop their full capacity. For example, in one series of tests nickel electrode utilization averaged 78 percent after cycle one, 88.5 percent after cycle 11, and 93.5 percent after cycle 20.

Nickel electrodes were able to be loaded in excess of 2.5 g/cc void. However, the useful upper limit was found to be 2.35 g/cc void in order to avoid plate thickening and blister formation (34). This limit of 2.35 g/cc void is recalculated to be 1.9 g/cc void after formation, cleaning, and thickening. The major contribution to this change is the reported (32) ten to twenty percent typical loss of active material following formation cycling. This is a relatively large change, but could be acceptable provided the change is consistent and predictable. More information is needed on this phenomenon.

Typical impregnation time histories are shown in Figure 2-24. Loading level rises nearly linearly and then plateaus at about 2.3 g/cc void. Cell voltage also rises as the cell approaches its loading limit. Note also that the plates with the highest loading had some surface deposited material, evidence of

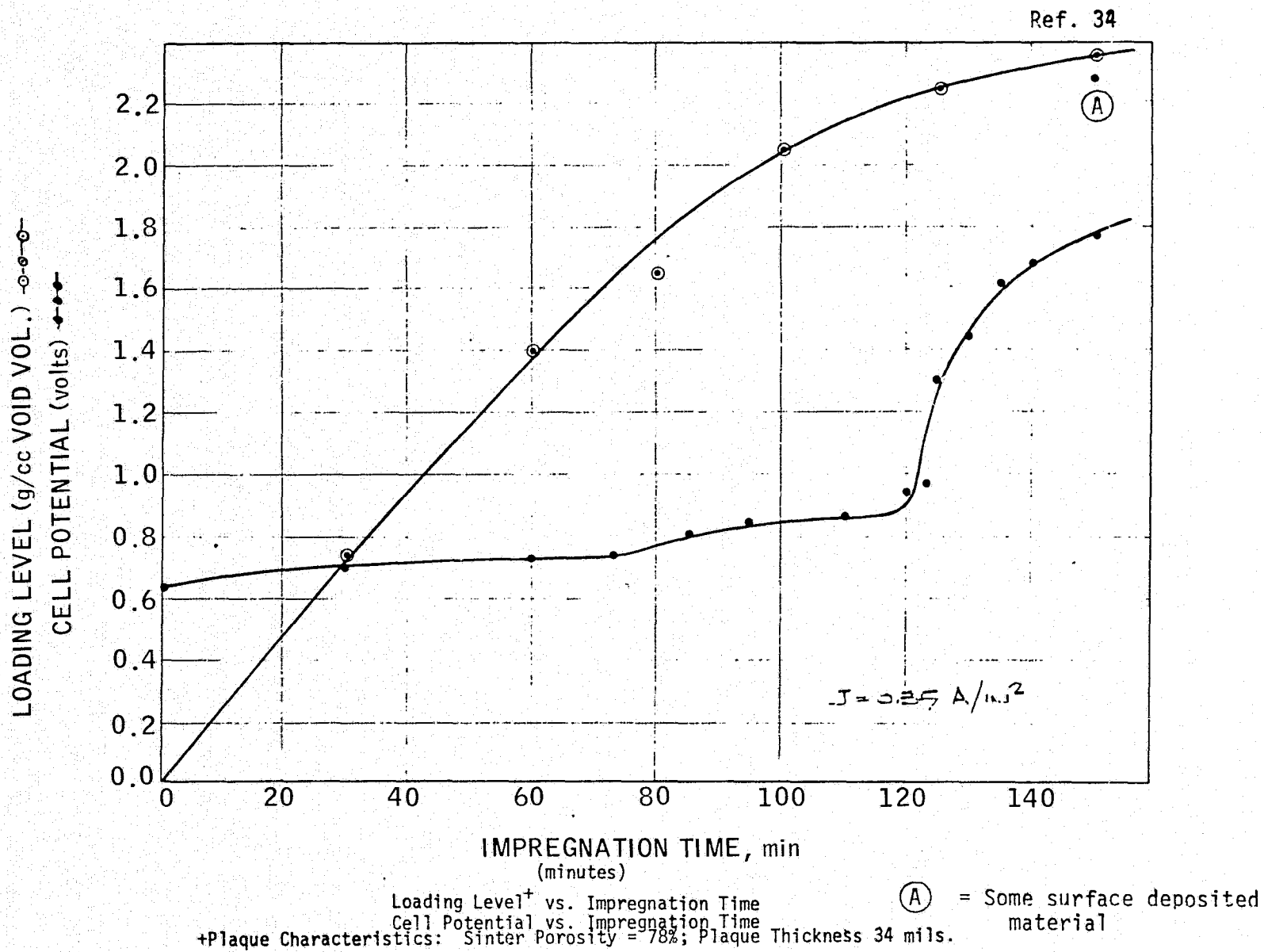
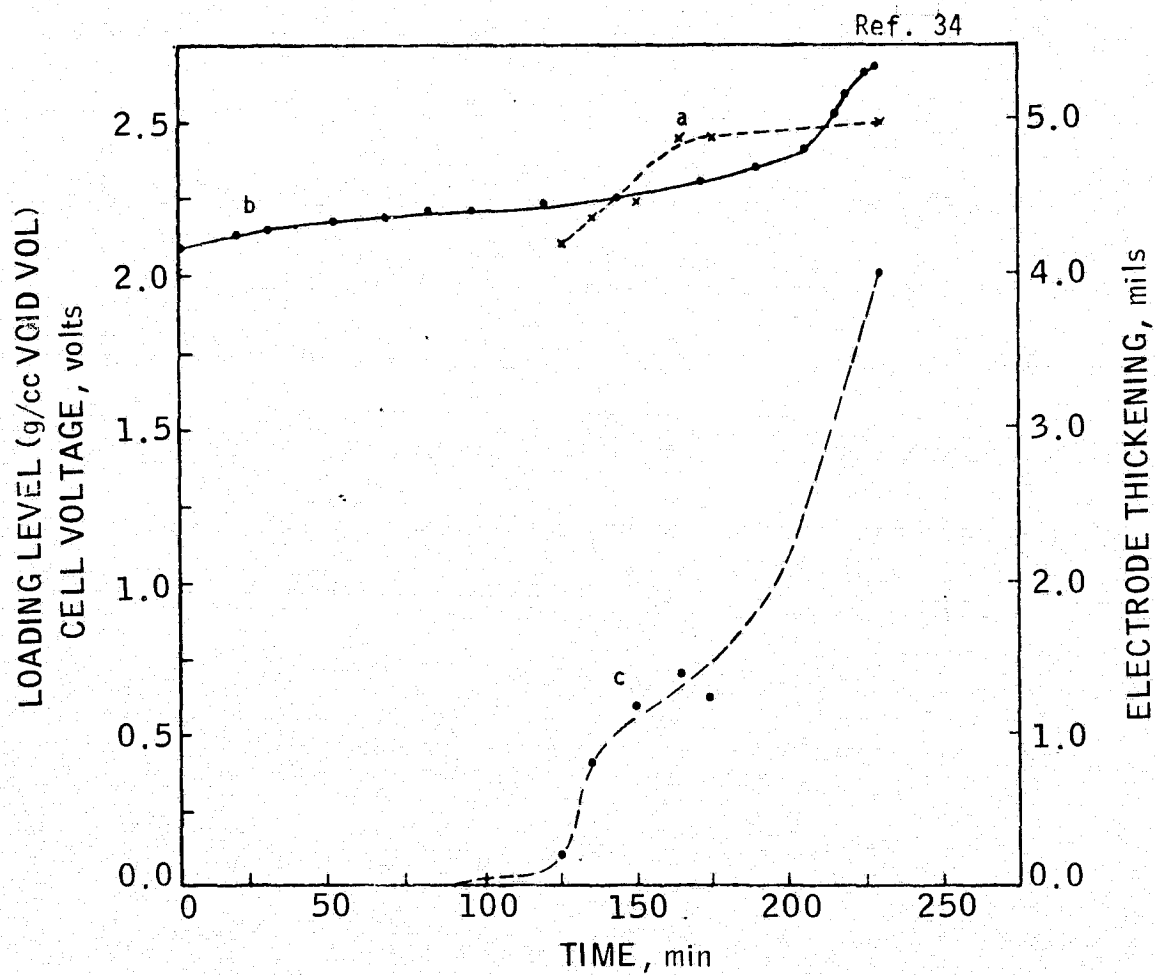


Figure 2-24: Typical Impregnation History of Nickel Electrodes

unsatisfactory impregnation. Surface deposition was a concern only at loading levels greater than 2.1 g/cc void. Plate thickening also starts at about 2.1 g/cc void, and becomes significant as the maximum loading is approached (Fig. 2-25). Typical plate thickening data are given in Table 2-3, based on 34 mil plaques of 82 percent porosity. Thickness increased approximately one mil from electrochemical impregnation, and an additional 0.7 mil following formation.

A hypothesis is presented in Ref. 33 attributing blistering on nickel positive electrodes to density changes of active material, and relating this to loading level. Data in Ref. 32 is summarized in Table 2-4, giving the blistering rate for three cell designs using electrochemical impregnation. These cell designs differ in the way the sinter is made, in the electrode thickness, and in the loading level. Blistering was greatest in cell design 11, which was thinnest and consequently had the highest loading in terms of grams per cc of void. Blistering in this design, with 2.65 grams/cc void, appears to be due to having exceeded the design upper limit of 2.35 grams/cc void. The role of other design parameters is not obvious from the data. Differences in the amount of cobalt additive would be important, but these data are not reported. Sinter strength would also have been a worthwhile measurement to help interpret blistering experience. Additional data on blistering is given in Table 2-5. In agreement with other work, blistering occurred on heavily loaded plates, whereas those loaded to 2.2 gm/cc void did not blister. There is also evidence from these data that plates loaded at high current density ( $0.5 \text{ A/in}^2$ ) blister more than those loaded at the nominal density current density ( $0.35 \text{ A/in}^2$ ). Other tests (35) showed that blistering occurred on plates that had been loaded at non-uniform current density, with blisters occurring near plate edges where current density was high. It is not known, however, whether this is due to the



POSITIVE ELECTRODE IMPREGNATION:

- (a) Loading level vs process time
- (b) Cell voltage vs process time
- (c) Electrode thickening vs process time

Figure 2-25: Nickel Electrode Thickening During Impregnation

Table 2-3: POSITIVE ELECTRODE<sup>Δ</sup> THICKNESS DATA

Impregnation Time (minutes)	Plate No.	Tare Thickness (mils)	Thicken. Following		Loading Level	
			EI <sup>Ø</sup>	Formation	(gNi(OH) <sub>2</sub> /cc void) EI <sup>Ø</sup>	Formation
230	45*	34.2	4.7	3.9	2.56	1.94
	46	<u>33.9</u>	<u>2.8</u>	<u>2.2</u>	<u>2.48</u>	<u>1.99</u>
	$\bar{X} =$	<u>34.0</u>	<u>3.8</u>	<u>3.0</u>	<u>3.52</u>	<u>1.96</u>
175	60	34.3	1.1	0.9	2.53	2.15
	61	33.7	0.9	0.9	2.48	2.02
	62	34.0	2.0	0.4	2.45	2.12
	63	33.9	1.6	0.8	2.40	2.05
	64	33.7	1.5	1.0	2.46	2.08
	65	33.3	1.1	0.8	2.36	2.02
	66	33.6	1.1	1.1	2.42	2.06
	69	34.3	0.7	0.0	2.33	2.09
	71	34.3	1.1	1.5	2.41	2.04
	72	33.4	1.3	1.6	2.44	2.05
	73	34.0	0.7	0.7	2.26	1.95
	74	34.2	0.9	0.6	2.36	2.04
	75	33.8	1.2	1.3	2.44	2.06
	77	34.3	0.9	0.5	2.29	1.98
	78	34.1	0.5	0.4	2.21	1.95
	79	33.6	1.4	0.9	2.29	1.98
	80	34.2	0.7	0.2	2.22	1.98
	81	33.9	0.7	0.7	2.11	2.02
	84	33.8	1.2	0.7	2.42	2.10
	86	33.9	1.2	0.0	2.22	1.97
	87	33.5	1.0	0.4	2.38	2.09
	88	33.2	1.0	0.6	2.41	2.08
	89	33.5	0.8	0.8	2.27	1.96
	90	34.2	0.5	0.6	2.28	2.01
	91	34.2	0.7	0.6	2.29	2.01
	93	33.9	1.8	0.5	2.25	1.99
	94	34.4	0.7	0.1	2.26	2.04
	96	34.2	0.6	0.3	2.34	2.09
	99	34.4	1.2	0.6	2.31	2.03
	120	<u>33.8</u>	<u>0.6</u>	<u>0.4</u>	<u>2.21</u>	<u>1.96</u>
	$\bar{X} =$	33.9	1.0	0.7	2.34	2.03
150	55	33.5	1.2	0.7	2.26	1.95
	56	33.9	1.8	0.2	2.22	1.94
	57	34.1	0.7	0.9	2.34	2.00
	59	<u>33.7</u>	<u>1.1</u>	<u>0.9</u>	<u>2.29</u>	<u>1.94</u>
	$\bar{X} =$	33.8	1.2	0.7	2.28	1.96
135	49	34.5	1.5	0.0	2.23	1.98
	52	<u>34.0</u>	<u>1.2</u>	<u>0.8</u>	<u>2.22</u>	<u>1.88</u>
	$\bar{X} =$	34.2	1.4	0.4	2.22	1.93

Δ nominal 3/4 mil, 82 percent sinter porous plaque electrodes

\* blistered during formation

Ø EI = electrochemical impregnation

+ corrected for plate thickening

Ref. 34

Table 2-4: EFFECT OF LOADING AND OTHER FACTORS ON NICKEL  
ELECTRODE BLISTERING RATE

	Ref. 32		
	Cell Design 6	Cell Design 11	Cell Design 15
Sinter Formulation (weight percent)*			
Polyox	44.4	3.5	3.5
Ni Powder	50.9	79.9	79.9
Oxamide	4.7	16.6	16.6
Sinter Fabrication			
Void volume (cc void/in <sup>2</sup> )	0.44	0.388	0.451
Sinter porosity (percent)	82.	85.4	85.4
Electrode area (in <sup>2</sup> )	17.52	17.52	17.52
Electrochemical Impregnation			
Thickness before formation (mils)	35.5	30.5	34.5
Thickness after formation (mils)	36.5	--	35.9
Impregnation current density (A/in <sup>2</sup> )	0.35	0.35	0.35
Initial weight gain (grams)	17.4	18.0	16.8
Loading (gm/cc void)**	2.25	2.65	2.13
Blistering Rate (Percent)	0	9.0	<1.0

\*Excludes water and methyl alcohol

\*\*Calculated, before formation

TABLE 2-5: BLISTERING DURING FORMATION OF  
ELECTROCHEMICALLY IMPREGNATED NICKEL ELECTRODES

Plate No.	Loading Current Density A/IN <sup>2</sup>	Loading Level g/cc void	Charge		Discharge		Utilization (%)	Final Thickness (mils)	Blistering During Formation
			Current (A)	Time (min)	Current (A)	Time (min)			
3-4	0.50	2.16	1.16	36	0.58	53.7	99	36.0	no
4-4	0.35	2.05	1.16	36	0.58	54.1	105	34.9	no
3-5	0.50	2.22	1.26	36	0.63	56.0	114	35.7	yes
4-5	0.35	2.24	1.26	36	0.63	55.6	112	35.4	no
3-6	0.50	2.35	1.32	36	0.66	49.3	102	35.5	yes
4-6	0.35	2.35	1.32	36	0.66	52.1	98	36.0	yes

high current density itself or to the resulting high loading in those regions. If indeed blistering is related to current density, then that would not only give guidance in avoiding blisters, but also would be concrete evidence that important life-related differences can occur from the manner of electrochemical impregnation as well as the level of impregnation.

Negative electrode investigations included use of 75 and 82 percent porosity plaque. Plaques that were 75 percent porous could be loaded to 2.0 grams  $\text{Cd(OH)}_2$  per  $\text{cm}^3$  void, whereas plaques that were 82 percent porous could be loaded to 2.4 g/cc void. One finding was that conditions that were optimum for loading a 75 percent porous plaque were not optimum for 82 percent porous plaque. This is consistent with the findings of others, that electrochemical loading behavior is very sensitive to variables which interact in a complex way; impregnation can be easily upset if all variables are not closely controlled. One of the variables that required adjustment in the change from 75 to 82 percent porous plaque was a reduction in current density from 2.0 to 1.6  $\text{A/in}^2$ . Another important finding was that there were significant differences between small beaker level tests and pilot plant operation. For example, a beaker test required 165 minutes for the end-of-loading voltage rise on a nickel plate (82% porosity, 32 mils thick, 0.35  $\text{A/in}^2$ ), whereas only 125 minutes were required with the pilot plant.

Loadings on negative plates were greater with two impregnation cycles (2.2 g/cc void) than with only a single cycle (2.0 g/cc void). This is possible because material blocking pores near the surface is removed by plate formation cycles. A problem with multiple impregnation cycles, however, is that a greater amount of plaque corrosion can occur.



The cadmium negative electrode has proved to be more difficult to impregnate and properly control than the nickel positive electrode. The problem is not only to obtain high levels of impregnation, but also to do this consistently. One of the methods investigated to improve impregnation of the cadmium electrode is the use of unsymmetric alternating current pulses (17,35). The work done must be viewed primarily as exploratory development firstly because the number of additional variables to be investigated is large, and secondly because we do not yet have a good understanding of why one condition works and why another does not. Clear answers were not obtained from this work, except that highest loadings generally occurred with alternating current pulses asymmetric with respect to time. Under such a system, the time permitted for the forward pulse is greater than the time for the reverse pulse. The optimum appears to be near 100 Hz (Table 2-6), though there seems to be a scatter in the loading data which confuses the effects of frequency. Not enough work was done to determine whether alternating current methods gave more or less consistent results than obtained with constant current.

It is not fully understood why the use of alternating current generally produces the greater loading of the cadmium electrode. This question is made more complicated by the fact that the highest loadings reported were obtained with constant current, the maximum being 3.14 gm/cc void (Table 2-7). On theoretical grounds, one would expect greater throwing power and electropolishing effects, helping penetration into the pores. Another possibility is the removal of passivating layers on the cadmium anode. As the cadmium anode corrodes, a film of basic cadmium salt forms on the surface, causing dissolution of cadmium to be slowed down and probably also making dissolution non-uniform. There was some evidence that this film was not present as much with the alternating current methods, although reference electrode or voltage

Table 2-6: ELECTROCHEMICAL IMPREGNATION OF 75 PERCENT POROUS SINTERED  
NICKEL PLAQUE\* TO MAKE Cd/Cd (OH)<sub>2</sub> ELECTRODES\*\*

Ref. 17

Plate No.	Electrochemical Impregnation Technique	Impregnation Time (Min.)	Current Density (A/in <sup>2</sup> )	Loading Levels (g/cc Void)	Thickening (Mils.)
2	CCS	12	1.4	1.87	0
4	CCS	12	1.6	1.77	0
3	CCS	12	1.8	1.93	0
6-1	CCS	3	2.0	1.28	0.0
6-2	CCS	5	2.0	1.42	0.1
6-3	CCS	7	2.0	1.73	0.0
6-4	CCS	9	2.0	1.80	0.3
6-5	CCS	11	2.0	1.89	0.0
6-6	CCS	13	2.0	2.02	0.3
6-7	CCS	15	2.0	1.95	0.6
11	ACP - 10 cps	12	2.0	0.45	-1.9
10	ACP - 50 cps	12	2.0	0.29	-0.2
22	ACP - 50 cps	12	2.0	0.08	-1.3
12	ACP - 75 cps	12	2.0	1.01	-0.6
9	ACP - 100 cps	12	2.0	1.65	-0.2
13a	ACP - 130 cps	12	2.0	0.29	-0.1
13b	ACP - 130 cps	12	2.0	0.46	-1.3
14	ACP - 100 cps	24	2.0	0.25	-0.2
<p>*Heliotek plaque, nominal 26 mil.; 75% sinter porous; void volume = 0.275 cc void/in<sup>2</sup> plaque  **Plate area 5.0 in<sup>2</sup>; CCS = constant current step; ACP = alternating current pulse</p>					

Table 2-7: ELECTROCHEMICAL IMPREGNATION OF 82 PERCENT POROUS SINTERED  
NICKEL PLAQUE\* TO MAKE Cd/Cd (OH)<sub>2</sub> ELECTRODES

Ref. 17

Plate No.	Electrochemical Impregnation Technique	Impregnation Time (Min.)	Current Density (A/in <sup>2</sup> )	Loading Level (g/cc Void)	Increase in Thickness (Mils.)
M-11	CCS	13.5	1.5	2.00	0
M-2	CCS	12	1.6	2.18	0
M-4	CCS	14	1.6	3.14	7
M-5	CCS	12	1.7	1.99	0
M-3	CCS	12	1.8	2.78	4
M-1**	CCS	12	2.0	1.92	-1
M-7	ACP - 100 cps	12	1.6	<0.5	-3
M-9	ACP - 75 cps	12	1.6	0.99	-1
M-10	ACP - 50 cps	12	1.6	<0.5	-1
M-12	ACPT - 11 cpm - 8:1	12	1.6	2.35	1
M-21	ACPT - 11 cpm - 8:1	12	1.6	2.27	1
M-24	ACPT - 11 cpm - 8:1	12	1.6	2.26	0
M-25	ACPT - 11 cpm - 8:1	12	1.6	2.32	2
M-26	ACPT - 11 cpm - 8:1	12	1.6	2.31	1
M-14	ACPT - 110 cpm - 3:1	12	1.6	2.49	2
M-16	ACPT - 1100 cpm - 8:1	12	1.6	2.30	5
M-17	ACPT - 11,000 cpm - 8:1	12	1.6	2.38	0
*Plaque characteristics: Marathon plaque; sinter porosity = 82 percent, 25 mil. thick; W = 0.290 cc void/in <sup>2</sup> plaque.					
**Scrubbing removed sinter					

CCS = constant current step; ACP = alternating current pulse; ACPT = alternating current pulse  
asymmetric with time

difference measurements are not available to help define behavior. It should be noted that film formation is not a problem with methods that use an inert anode rather than a cadmium anode. One of the few other instances in which alternating current was used previously is the work by Kober (26) impregnating the nickel electrode using an ammine nickel formate solution. From the use of alternating current he was able to obtain an impregnation level that was a linear function of time. It is clear that a better understanding is needed of the physical effects of alternating current impregnation if full advantage is to be taken of the possibilities of this approach.

Utilization of negative electrode active material could not be determined accurately because some corrosion of the plaque occurred. Estimates of utilization after impregnation (32) were 85 to 90% theoretical for the constant current loading method, 85% for the alternating pulse current pulse method, and 80% to 92% for the asymmetric alternating current pulse method. A utilization of 80% was used for cell design purposes, and is apparently a slightly conservative value. In one test with cadmium electrodes flooded under negative-limited conditions, utilization remained nearly constant after 750 full discharge cycles (Fig. 2-26). This is good evidence of a very stable electrode design.

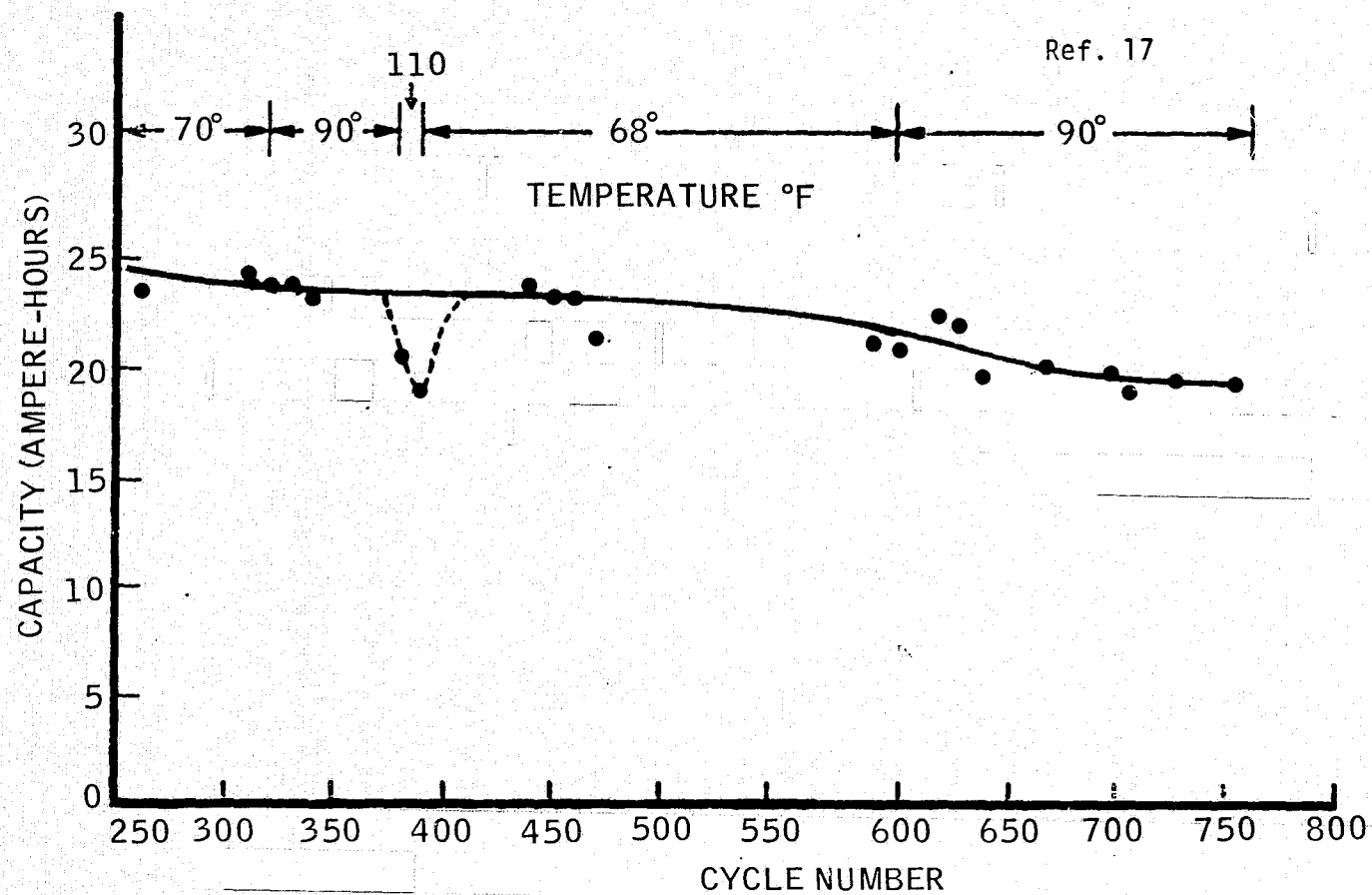


Figure 2-26: Capacity of Electrochemically Impregnated Negative Limited Cells During 100% DOD Cycling

### Seiger and Puglisi's Work -- Yardney

Building on the work done at Heliotek/Spectrolab, Seiger and Puglisi have refined the methods for electrochemical impregnation of nickel and cadmium electrodes. The process used for manufacture is based in part on the method of Pell and Blossom (37). The Pell and Blossom method uses a high temperature aqueous system, an inert counter electrode, Carbowax as a wetting agent, pH in the range of 1 to 3, and a constant potential cathodization, typically 3.5 volts versus a reference electrode such as Ag/AgCl. Pell and Blossom only reported work on the nickel electrode.

Comparisons were made between the Yardney aqueous process and the Pickett alcoholic process for the impregnation of nickel electrodes (7). Plates from both methods were found to be mechanically stable, though the alcoholic method resulted in a 4% weight loss after the conduct of an accelerated test. Examination of the plate interior with scanning electron microscope showed that the deposited materials were evenly distributed for both methods, and that the crystalline structure was about the same; this structure is much different than that produced by Kandler, however (1). On lightly loaded plates, the active material utilization was a little less for the alcoholic method, but this may not be an intrinsic characteristic.

By means of calculations based on experimental data (38), the effects have been determined of impregnation level on capacity per unit weight (Fig. 2-27) and per unit volume (Fig. 2-28). Based on 35-mil plaque loaded to 2.0 g/cc void, the optimum on a volume basis is 78 percent porosity, essentially in agreement with a prior calculation of 77 percent (33). The capacity per unit weight

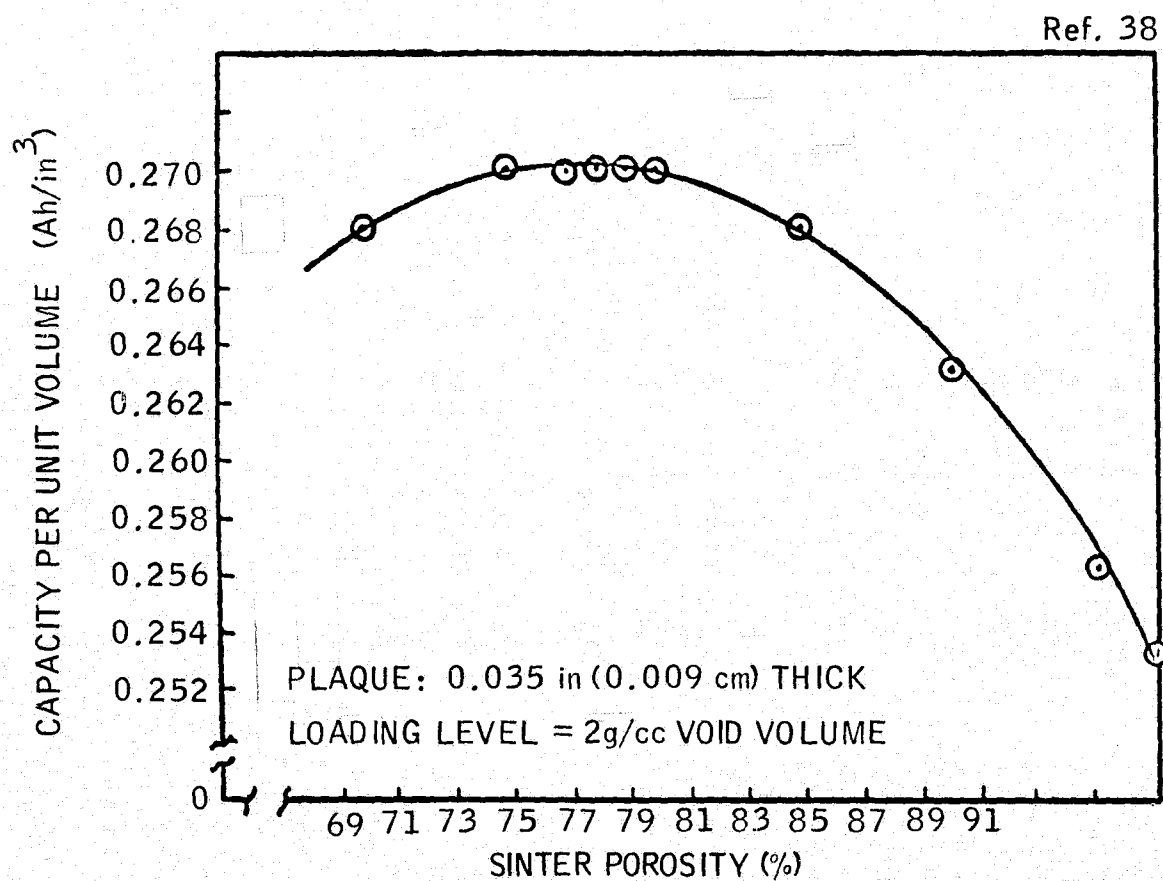


Figure 2-27: Effect of Electrochemical Impregnation Level on Capacity per Unit Volume

Ref. 38

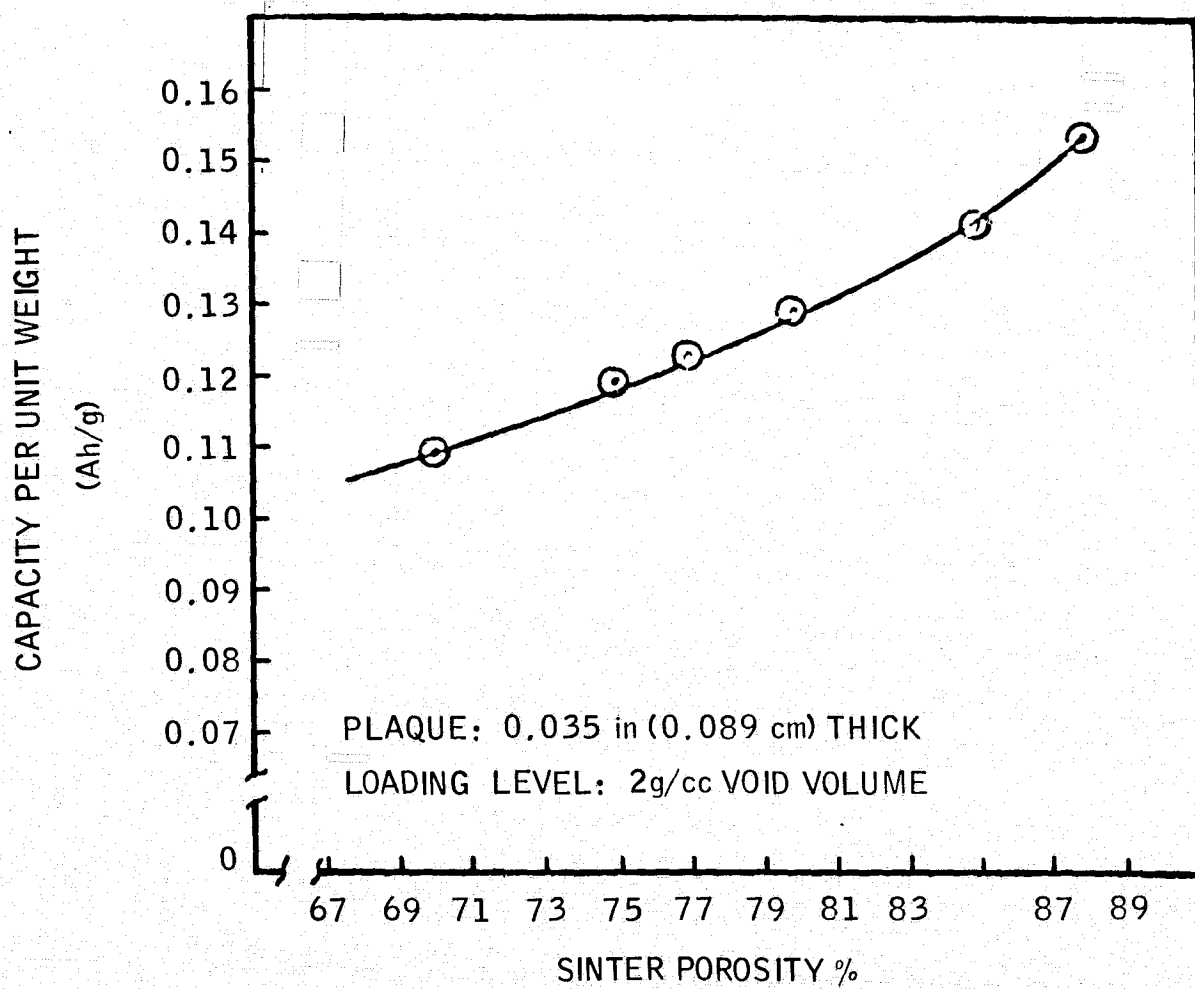


Figure 2-28: Effect of Electrochemical Impregnation Level on Capacity per Unit Weight



improves with increased porosity, so the porosity selected for a cell design would be a compromise between these two considerations; the best range is considered to be 78 percent to 83 percent.

When loading of a nickel electrodes is observed as a function of time (38), a point is reached when the electrodes begin to thicken (Fig. 2-29). As thickening progresses, the volumetric loading tapers off and eventually decreases. Thus, even though the electrode is heavier, it is less favorable on a volume basis.

Utilization of active material in the nickel electrode is found (38) to be highest at a loading level of 1.6 g/cc void (Fig. 2-30). The peak utilization of 1.40, based on a one electron transfer as theoretical, is one of the highest values ever reported for the nickel electrode. The reasons for such a peaked characteristic are not reported. It should be noted that even though utilization is reduced above 1.6 g/cc void, the volumetric capacity does not change much in the range of 1.6 to 1.9 g/cc void. In Puglisi's example (38), it was essentially constant in that range; in Seiger's example (5), there was a modest reduction in that range (Fig. 2-31).

Seiger (6) impregnated a variety of cadmium electrodes using slurry-made plaque from both Inco type 287 and type 255 powder. Porosities ranged from 75 to 91 percent, and thicknesses ranged from 25 to 40 mils. Two molar cadmium nitrate at pH of 2 to 4 was used, and the impregnating solution was made to flow tangential to the electrode surfaces. Corrosion was determined to be less than one percent.

Ref. 38

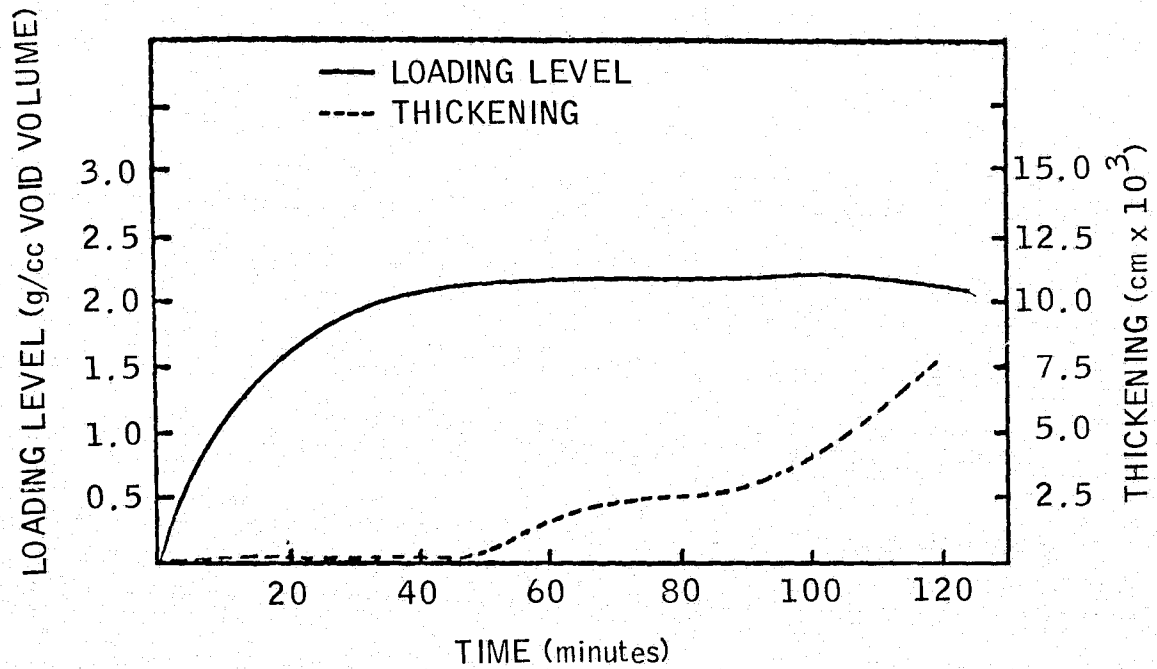


Figure 2-29: Thickening and Loading Level Changes During Electrochemical Impregnation of Nickel Electrodes

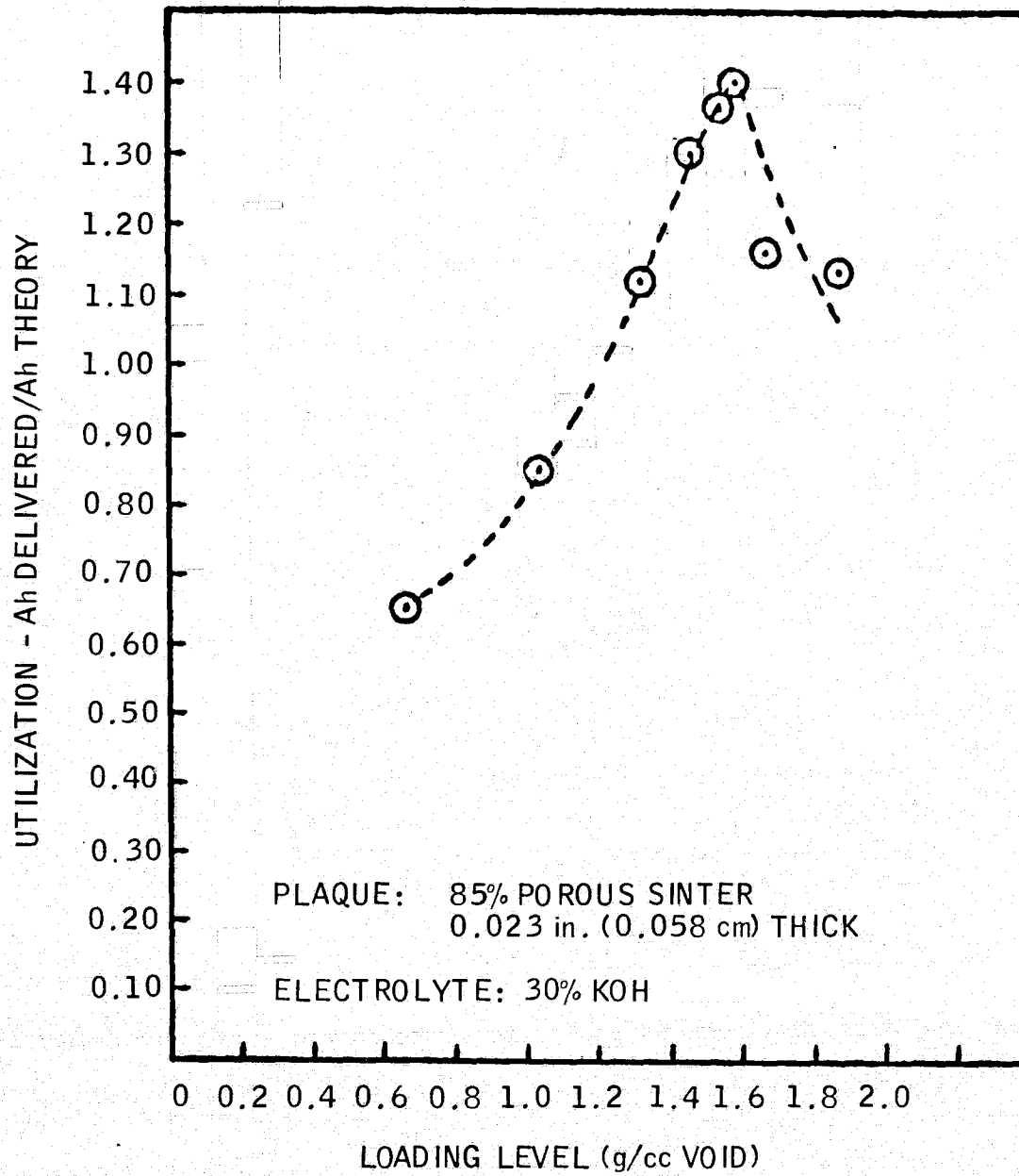


Figure 2-30: Effect of Electrochemical Loading Level on Utilization of Nickel Electrodes

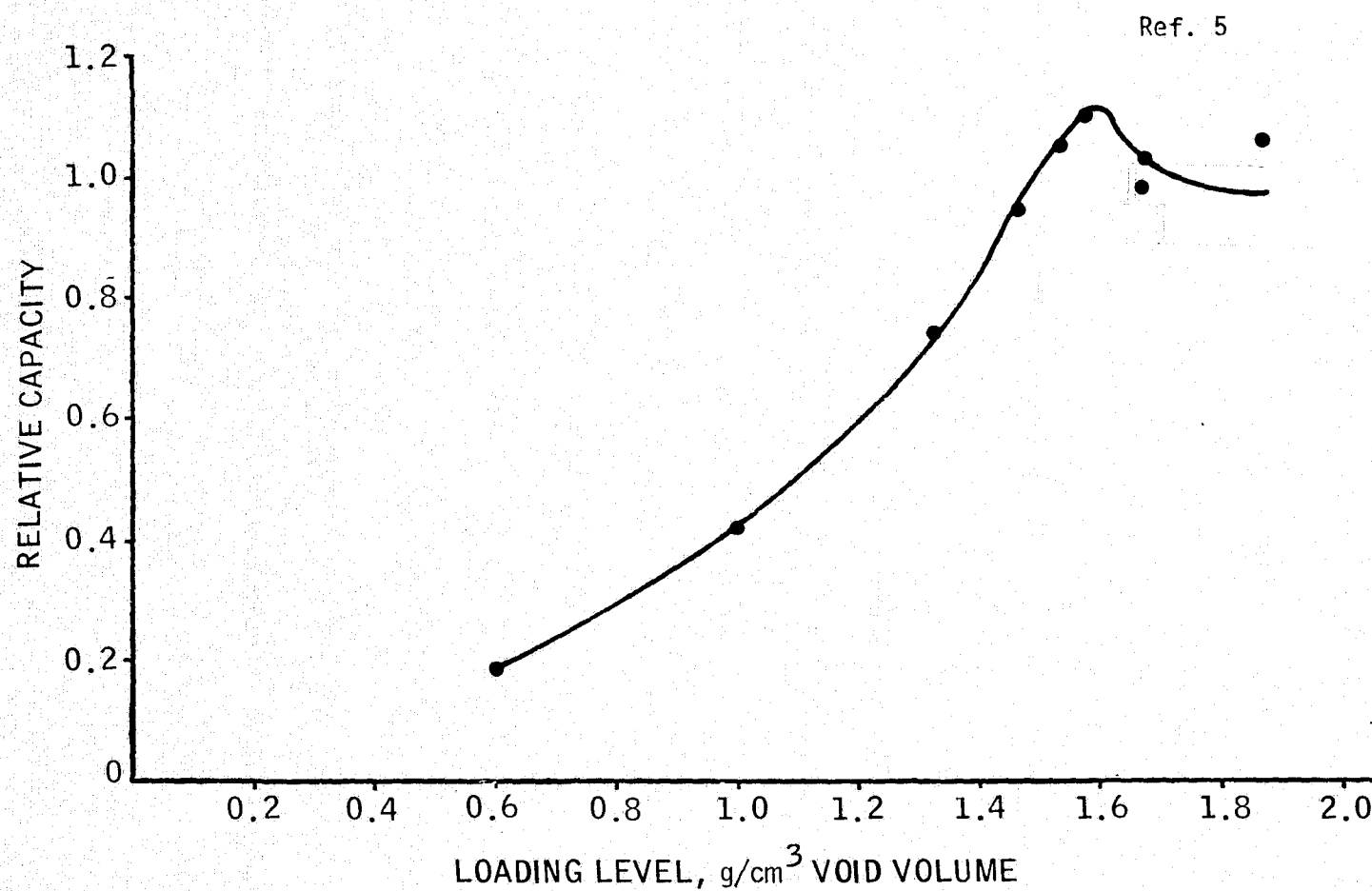


Figure 2-31: Capacity Dependence on Loading Level For Electrochemically Impregnated Nickel Electrodes

Some cadmium electrodes had utilizations of 94 percent, which is usually high. Scanning electron micrographs of such plates showed fine crystals about one micron in size. The inner region of the electrode was more highly impregnated than was the outer region, a feature just the opposite of that found in vacuum impregnation. These electrodes not only had extremely high utilization, but also had superior oxygen recombination ability, maintaining less than 44 psia with a continuous C/2 overcharge. Entrapped air was found to be more difficult to remove with such electrodes than with electrodes made by the vacuum impregnation method.

Nickel cadmium cells of 34 ampere-hour capacity have been built with Yardney's improved electrochemical impregnation process. These are now under test (39), and provide approximately 20 watt-hours/lb with stable performance. Second generation designs have been conceived (39) which use lighter cases and make other changes to improve the energy even further.

#### Pickett's Work

Pickett (13 to 20) has developed an impregnation process in which ethanol is added to the nitrate solution. The ethanol reacts to generate hydrogen ions and minimize pH changes, oxidizing to acetaldehyde, acetic acid and carbon dioxide. The ethanol helps wetting of the plaque and probably performs some other functions, for it is sometimes used as an additive in commercial electrochemical plating solutions. This is an important and successful work, and formed the basis for the work by Seiger and Puglisi at Heliotek; this work is now being continued by Hill at Eagle Picher. Pickett's work is well documented, and a summary report is to be published soon by WPAFB on his work.

A detailed description of his work is omitted here for those reasons and also to permit time available to report on lesser known or lesser available research by other workers.

#### Brent's Work

John Brent of McGraw-Edison Co. has used Pickett's process for electrochemical impregnation of nickel electrodes. This has been successful, yielding good plates with little or no change from published information and procedures. Cadmium electrodes could not be made successfully with published procedures, so a new electrochemical impregnation method has been developed at McGraw-Edison Co. Details are not available on this work.

#### Hill's Work

Jim Hill of Eagle-Picher Co. has done experimental work on electrochemical impregnation using Pickett's process. Work is now progressing under WPAFB contract to build a manufacturing facility and produce nickel cadmium cells by electrochemical impregnation.

#### Rampel's Work

Guy Rampel of General Electric is developing an electrochemical impregnation process based on the method developed by Bell Laboratories. This undertaking is just getting started.

#### Stephenson's Work

Robert Stephenson of Motorola has developed an electrochemical impregnation process (51) using boiling solutions of nickel or cadmium nitrate. Formic acid is added to the solution, reacting with oxide layers on the electrode and raising the pH from one to four. This is an important development, for it is in continuous commercial operation, having produced many quality high-rate cells.

### 3.0 ELECTROCHEMICAL DEPOSITION EXPERIENCE

#### Edison's Work

It is primarily of historical interest to note that Edison appears to have been the first to use electrochemical methods of making nickel electrodes (40). A grid of nickel plated perforated steel was used as the cathode, with nickel anodes. The electrolyte used was a ten percent aqueous solution of nickel nitrate. An alternative electrolyte was an aqueous mixture of nickel sulfate and ten percent of sodium nitrate, which act as oxidizing and plating agents. Nickel hydroxide was electrolytically deposited on the nickel plated steel cathodes. The electrodes were washed, and were then ready for use in batteries.

#### Mueller's Work

Mueller has developed a process (41) for electrodeposition of cadmium sponge on metal matrix, such as nickel screen, perforated metal or expanded metal. This process is an especially important one, for it has been reduced to practice and is in production at Gould, Inc.

The process uses a sacrificial cadmium anode in the form of rods. The electrolyte is an aqueous solution of cadmium nitrate and nitric acid, with pH held between 1.0 and 1.5 and a temperature of 20°C. The deposit which forms is a mixture of cadmium hydroxide and nitrogenous compounds. This complex is charged in 30% KOH against an inert anode such as nickel at a current density of 0.03 to 6.0 A/in<sup>2</sup>, producing spongy cadmium. While still wet, the electrodes are rolled at about 500 psi to reduce the sponge to about 1/3 of its original thickness. The spongy cadmium is then discharged to cadmium hydroxide, using a current density equal to or slightly lower than used previously for charging. The final operations are a 4 or 5 minute wash with hot water to remove nitrogenous compounds, then air drying.

#### Mueller's Work (Cont'd)

During deposition, the sacrificial cadmium anode becomes coated with a white deposit consisting of a complex of cadmium oxide and cadmium nitrate. This complex is redissolved in the acid electrolyte, so the cadmium nitrate in the solution does not become depleted.

Electrodes prepared in this way typically had 40 by 40 nickel mesh substrate and a final thickness of 0.020 inches. Rolling is claimed to make the plates stronger and minimize sluffing off of active material.

#### Jost's Work

Jost (42) developed an electrochemical method of depositing cadmium on a thin grid of expanded nickel mesh. The electrolyte was cadmium nitrate,  $\text{Cd}(\text{NO})_3 \cdot 4\text{H}_2\text{O}$ , at a concentration of 350 grams nitrate per 150 ml of water. Using a 7 mil, 0.848 gm mesh with 3.4 in<sup>2</sup> projected area, the electrode enlarged after cadmium deposition to 20 mils with a weight gain of 3.554 g cadmium, and had a utilization greater than 70% in repetitive cycling. Electrodes of this type are of extremely high energy density, and were stable under repetitive cycling. Electrodes of this kind would very likely be suited to relatively short life, high energy density nickel cadmium cells.

#### Black's Work

Black and coworkers (43) developed electrochemical deposition methods to make both nickel and cadmium electrodes. These processes were developed sufficiently to build flexible nickel cadmium batteries for use in scientific balloons. The flight batteries had a capacity of only 80 mAhr, and had an



### Black's Work (Cont'd)

energy density of 1 to 5 WHrs/lb; it is significant that laboratory versions of these batteries reached 15 WHrs/lb.

Flexible, lightweight electrodes were made by first metalizing Dynel fabric with electroless copper. Cadmium electrodes were made by electroplating at room temperature with an aqueous solution of cadmium oxide, sodium cyanide and Rhoco brightener, using a current density of 20 A/ft<sup>2</sup>. Nickel electrodes were made by electroplating nickel over the copper plate, then electroplating nickel hydroxide at room temperature with a solution of nickel sulfate, nickel chloride, nickel ammonium sulfate and nickel formate. The pH was adjusted to 1.5 to 3.5 with sulfuric acid. An unusual current density profile was used, starting with 10 A/ft<sup>2</sup> and increasing step-wise to 50 A/ft<sup>2</sup>, then decreasing step-wise back to 10 A/ft<sup>2</sup>; the increase and decrease cycle then continued throughout the electroplating time.

### MacArthur's Work

MacArthur (25) prepared electrochemically deposited thin film nickel hydroxide electrodes in order to investigate their electrochemical properties. Capacity changes during cycling are shown in Figure 3-1. The decrease in capacity during the first few cycles is presumed due to the fact that alpha nickel hydroxide forms from the nitrate reduction, and then changes to the less hydrated beta nickel hydroxide which is not as efficient on discharge. The capacity increase from cycle 10 to 30 is presumed due to the formation on overcharge of gamma material. Capacity loss after cycle 30 is presumed due to stresses during cycling.

- BASIS:
- MacArthur, Ref. 25
  - ELECTROCHEMICAL DEPOSITION AT 100 mA  
FROM 0.5 M  $\text{Ni}(\text{NO}_3)_2$  SOLUTION
  - FILM THICKNESS CORRESPONDS TO  
TYPICAL COMMERCIAL ELECTRODE
  - CYCLING AT 1.0 C RATE
  - 20% OVERCHARGE

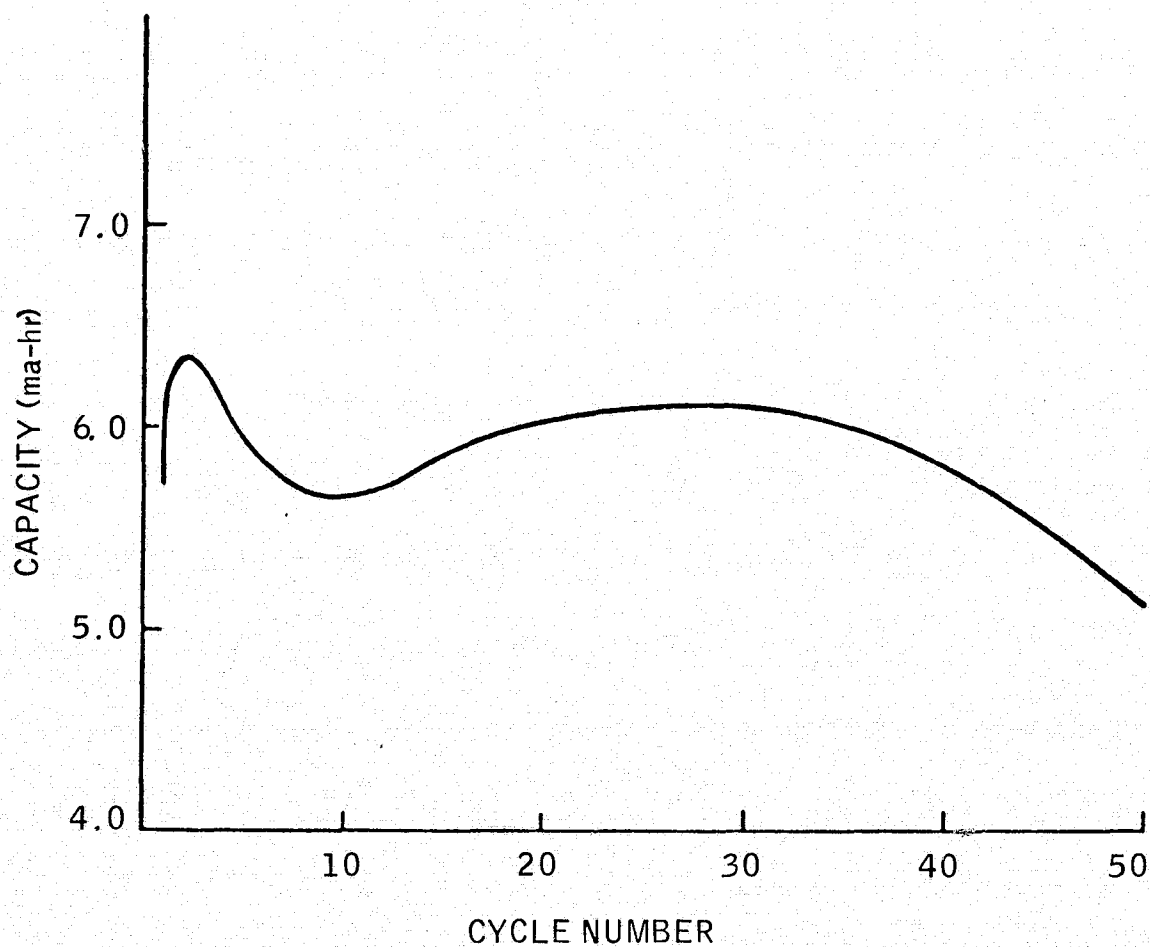


Figure 3-1: Effect of Cycling on Capacity of Thin Film Nickel Electrodes

MacArthur's Work (Cont'd)

The hypothesis that stresses during cycling cause a reduction in electrode capacity is given support by life cycling tests on electrochemically deposited thin film electrodes of differing thickness. Results are shown in Figure 3-2, in which capacity is a linear function of film thickness. Lifetime of the electrode is seen to decrease as the film is made thicker, presumably because of increased stresses on cycling.

Basis:

- o MacArthur, Ref. 25
- o Lifetime = number of cycles to reach half of max capacity
- o Electrochemically deposited thin film electrodes
- o Film thickness is linear function of capacity

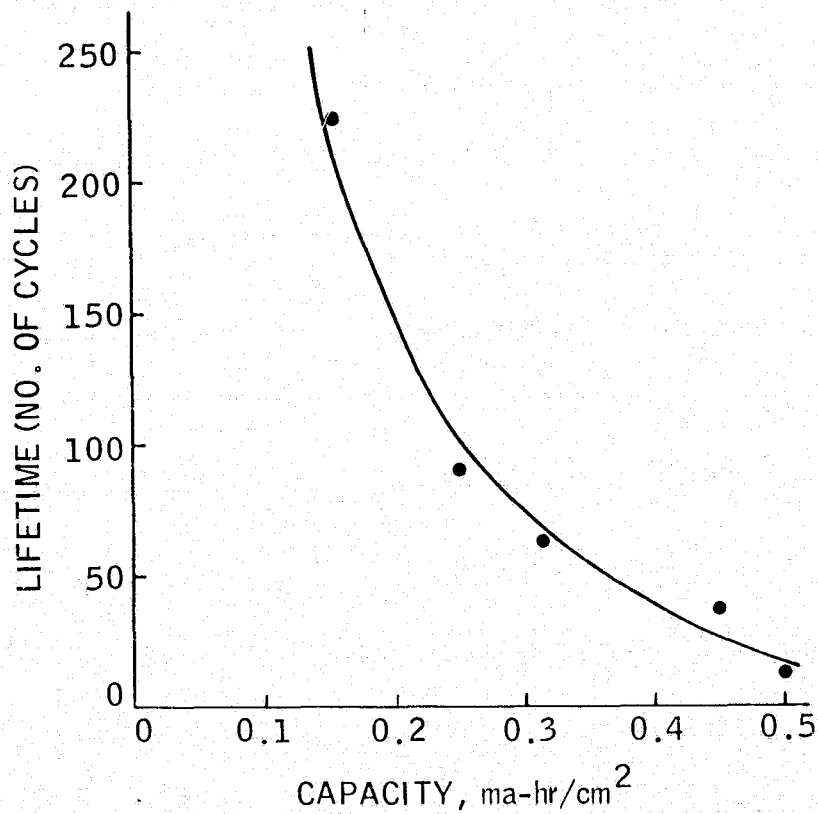


Figure 3-2: Effect of Capacity on Cycle Life of Thin Film Nickel Electrodes

#### 4.0 EFFECT OF ADDITIVES TO ELECTROCHEMICALLY IMPREGNATED ELECTRODES

##### Introduction

There is an extensive literature on the effects of additives to nickel cadmium cells, and no attempt is made here to review that body of information. The effects of additives can depend to some degree on the way the electrodes are made. Therefore, the purpose here is to focus on results conducted with electrochemically impregnated electrodes. Also, it is worthwhile to examine differences in conclusions on the optimum amount of additives, especially cobalt.

The question of effects of additives to the nickel electrode is made more complicated by the fact that most additives have a positive effect (44). Well controlled experiments are essential, preferably using production manufacturing equipment. Unfortunately, many manufacturing processes have poor reproducibility.

All investigations on the effects of additives to electrochemically impregnated electrodes have been with the nickel electrode. This is unfortunate, in that the cadmium electrode also undergoes important changes which might be made less harmful by the addition of additives. The practical reason for this, of course, is that very few investigators have succeeded in making a good, reproducible cadmium electrode.

##### Cobalt

Behavior of Cobalt. The beneficial effect of cobalt on the nickel electrode is well documented. Charge acceptance is increased, and discharge capacity at high temperature is maintained better during cycling. Another effect of cobalt additions is the ability to negate the harmful effects of some undesirable impurities. Silicon, for example, reduces the capacity of the nickel electrode during cycling. With the addition of cobalt, cycle life becomes essentially independent of silicon content (45).

The benefits of cobalt occur qualitatively for nickel electrodes irrespective of the manner of plate loading. The major questions that arise in the use of cobalt are: 1) Does cobalt's effectiveness depend in any way on the process used? 2) What fraction cobalt is the best to use? 3) What are the quantitative effects over a wide range of conditions, such as loading level, cobalt amount and cycling variables? Though this additive has been common for many years, good answers to these questions are not available.

Very little work has been done to relate the effectiveness of cobalt to the process used for its inclusion in the electrode. Weininger (44) conducted an experiment in which nickel and cobalt metals were codeposited electrolytically on nickel foil, using acidic sulfate solutions. Upon voltametric cycling in 0.2N KOH with triangular voltage sweep, he found two anodic peaks instead of only one. This was caused by isolated patches of  $\text{Ni(OH)}_2$  and  $\text{Co(OH)}_2$ . Although commercial electrodes are not made this way, this experiment demonstrated that electrochemical methods can result in only partial benefit from the cobalt.

Other precedents for incomplete utilization of the cobalt have also been observed, but with conventionally impregnated electrodes, not electrochemically impregnated ones. Yamashita (46), for example, found it was easy, based on color, to observe separation of the cobalt phase above 20 percent cobalt.

With electrochemically impregnated nickel electrodes, it has been found that the cobalt concentration in the electrode is essentially the same as that in the bath (18, 19). However, after cycling of electrodes with 10 to 12 percent cobalt (18, 19), a one or two percent loss of cobalt from the electrode has sometimes been observed. The final location of this lost material was not determined. Incidentally, one problem observed is that distinctions often are

not observed in the literature between percentages of cobalt and cobalt hydroxide. Often a stated percentage of cobalt should have been stated as cobalt hydroxide. Future investigators should be aware of this problem in attempting to correlate results by various workers.

One would expect that as the fraction of cobalt is increased, more of the properties of pure cobalt hydroxide would be exhibited, and the more important it becomes to learn about the chemistry and behavior of this additive. It has generally been regarded that any soluble species of cobalt are not harmful to nickel cadmium cells; this is probably true, though the point has not yet been proven. Both alpha and beta forms of cobalt hydroxide occur, and they behave differently, a point which can cause confusion with literature that does not make this distinction. Grube and Feucht (47) showed that  $\text{Co(OH)}_2$  dissolves in KOH solution with the formation of potassium cobaltate,  $\text{KCoO}_2$ . Boldin (48) showed that oxidation of such a solution forms the inert compound  $\text{CoHO}_2$  plus an unidentified species intermediate between  $\text{CoHO}_2$  and  $\text{KCoO}_2$  and which is reducible. Weininger (44) cycled 100%  $\text{Co(OH)}_2$  electrodes, and obtained good comparative information with 100%  $\text{Ni(OH)}_2$  electrodes. He determined, for example, that cobalt and nickel have essentially the same oxygen overvoltage potential, and that cobalt anodization has a higher degree of irreversibility than nickel.

The physical reasons for the benefits produced by cobalt additions are not well understood. Cobalt may lower the volumetric changes that occur, either from the charge-discharge process or from differential thermal expansion. Beauchamp (49) found spalling of active material to be more pronounced from nickel electrodes without cobalt, suggesting a volumetric effect. The improved charge acceptance, resulting in increased reversibility, is clearly an electrochemical effect and is evidenced by lower potential on charge during polarization scanning (44, 49, 50).

For example, Pickett (18, 19) obtained excellent charge efficiency in 100% DOD cycling tests at high temperature; by the addition of approximately 9% cobalt hydroxide, he obtained efficiencies of 94 to 95 percent at 37°C with flooded cells using electrochemically impregnated electrodes. Cycle life tests are now underway on cells with these electrodes.

Effect of Cobalt on Cycling. Weininger (44) tested electrochemically impregnated nickel electrodes with controlled amounts of cobalt ranging from 0 to 20%. These electrodes were only 10 mils thick, and had relatively low capacities, ranging from 0.8 to 3.2 AH/in<sup>3</sup>. These electrodes were cycled with a voltametric sweep method. Utilization of active material at 45°C is given in Figure 4-1 as a function of cobalt concentration, and the results suggest that nothing is to be gained by concentrations greater than 6%. Considering the large variation in capacity of the several samples, the low loading level, the high temperature of the test, and the thinness of the electrodes, it is remarkable that the results are in close agreement with typical commercial practice, which uses about 5% cobalt. Determination of the optimum design for aerospace cells would require tests more extensive than these, however.

Beauchamp and Maurer (49) tested the effect of various amounts of cobalt additive on nickel electrodes electrochemically impregnated according to the Bell Labs process, having 6 to 7 AH/in<sup>3</sup>. Most tests were with a 2C charge for one hour, giving 100% overcharge, then a C-rate discharge to 1.0 V. A few other tests used the 10C rate for charge and discharge and gave identical results.

A preliminary experiment was conducted using electrodes made from plaques that had been sintered at different temperatures, thus obtaining a range of sinter strength. This test gave results (Fig. 4-2) that were essentially independent of sinter strength. In another test in which nickel hydroxide loading was



Ref. 44

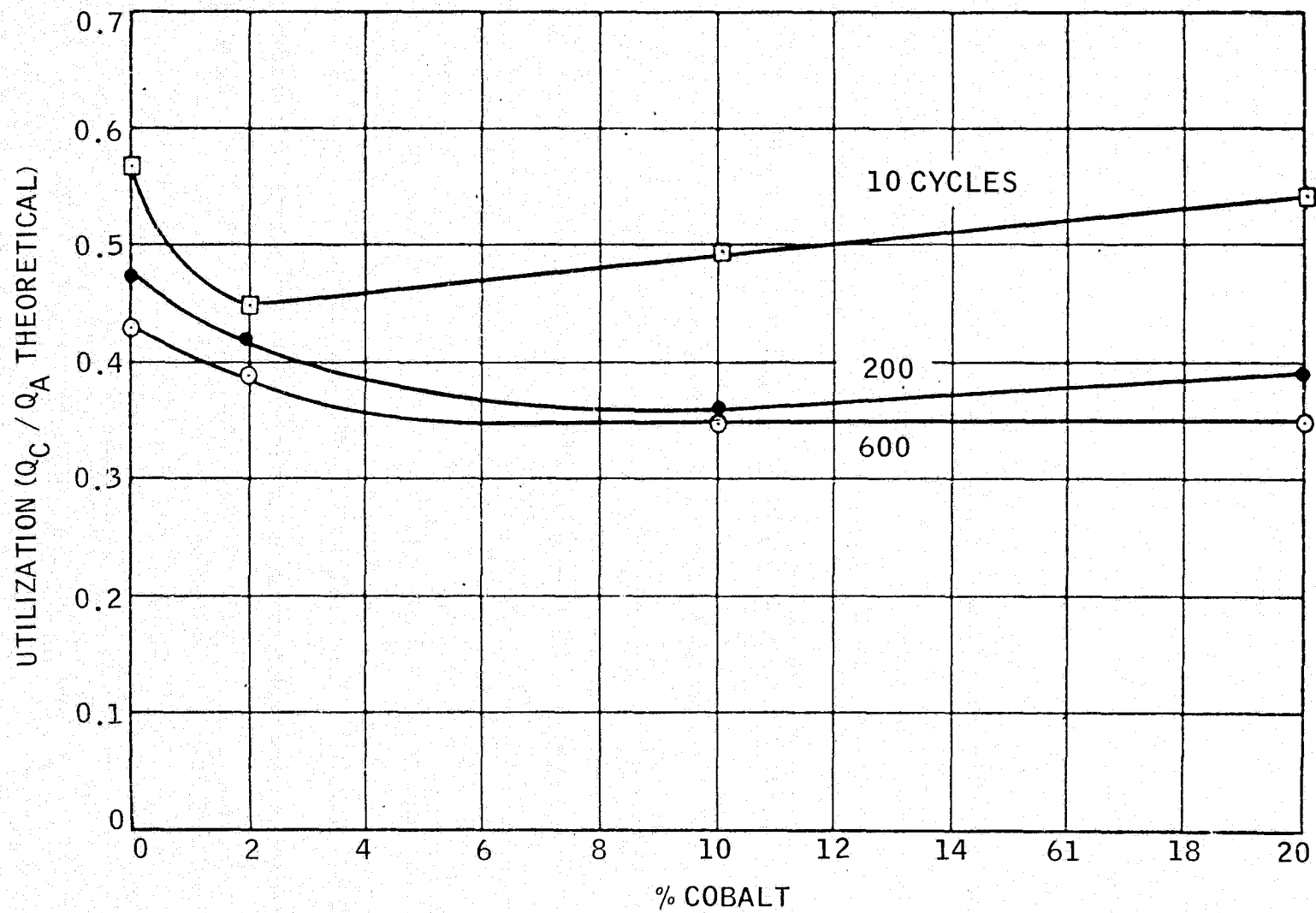


Figure 4-1: Utilization of Active Material as a Function of Cobalt Content and Cycle Life at 45°C

Ref. 49

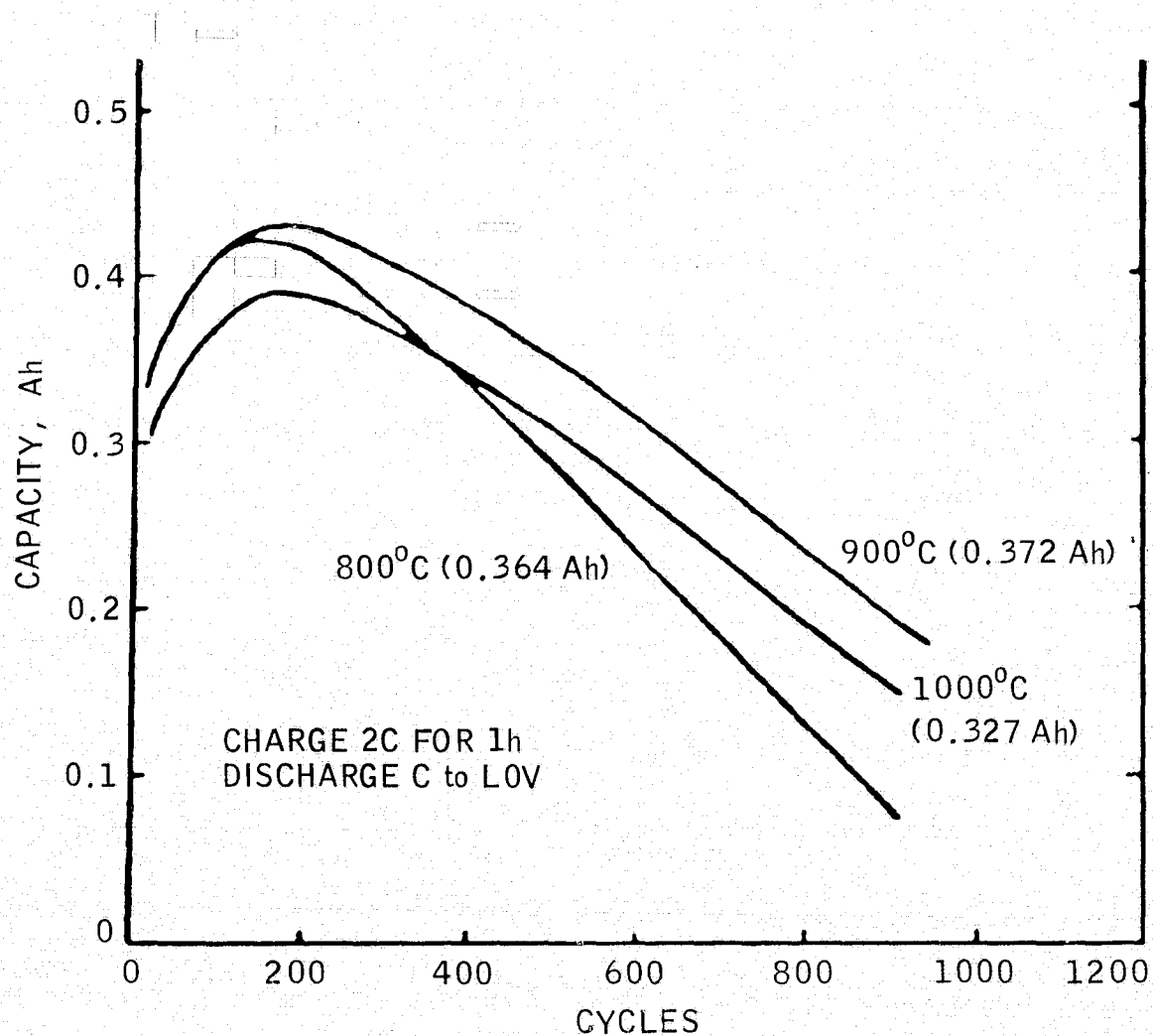


Figure 4-2: Effect of Sinter Strength on Nickel Electrode Cycle Life at 110°F

varied, results showed performance under repetitive cycling to be independent on loading (Figure 4-3). Thus, it could be concluded that the loss of cycle life is due to the active material itself.

Beauchamp and Maurer (49) found that addition of cobalt to the nickel electrode made significant improvements in cycle life at 75°F (Figs. 4-4 and 4-5) and 110°F (Fig. 4-6). At 20°F, however, little capacity fading was observed, so the addition of cobalt had only a slight effect (Fig. 4-7).

It should be noted from the test results of Beauchamp and Maurer that the initial capacities were lower in nickel electrodes without cobalt than for electrodes where cobalt was present. This may also be seen in Table 4-1 which reports the initial utilization of those electrodes. An unexplained finding in these tests is the lower surface area for cobalt-containing electrodes.

#### Cadmium

Cadmium is an important additive to the nickel electrode and is used commercially by at least two U.S. manufacturers. One of its functions is to provide a measure of reversal protection, and another is to reduce capacity fading during cycling. Weininger's tests on electrodes made by electrochemical deposition of active material on nickel foil substrates (44) show that cadmium additive reduces charge voltage, a phenomenon experienced also with cobalt. He found that cadmium extends the cycle life of nickel electrodes but is not as effective as cobalt is.

Beauchamp and Maurer (49) tested electrochemically impregnated electrodes and got results similar to Weininger's with nickel foil substrate. Their tests, conducted at 10C charge and discharge rates, showed that cadmium was decidedly helpful in reducing fading (Fig. 4-8), but not quite as effective as cobalt when tested under identical conditions (Fig. 4-5).

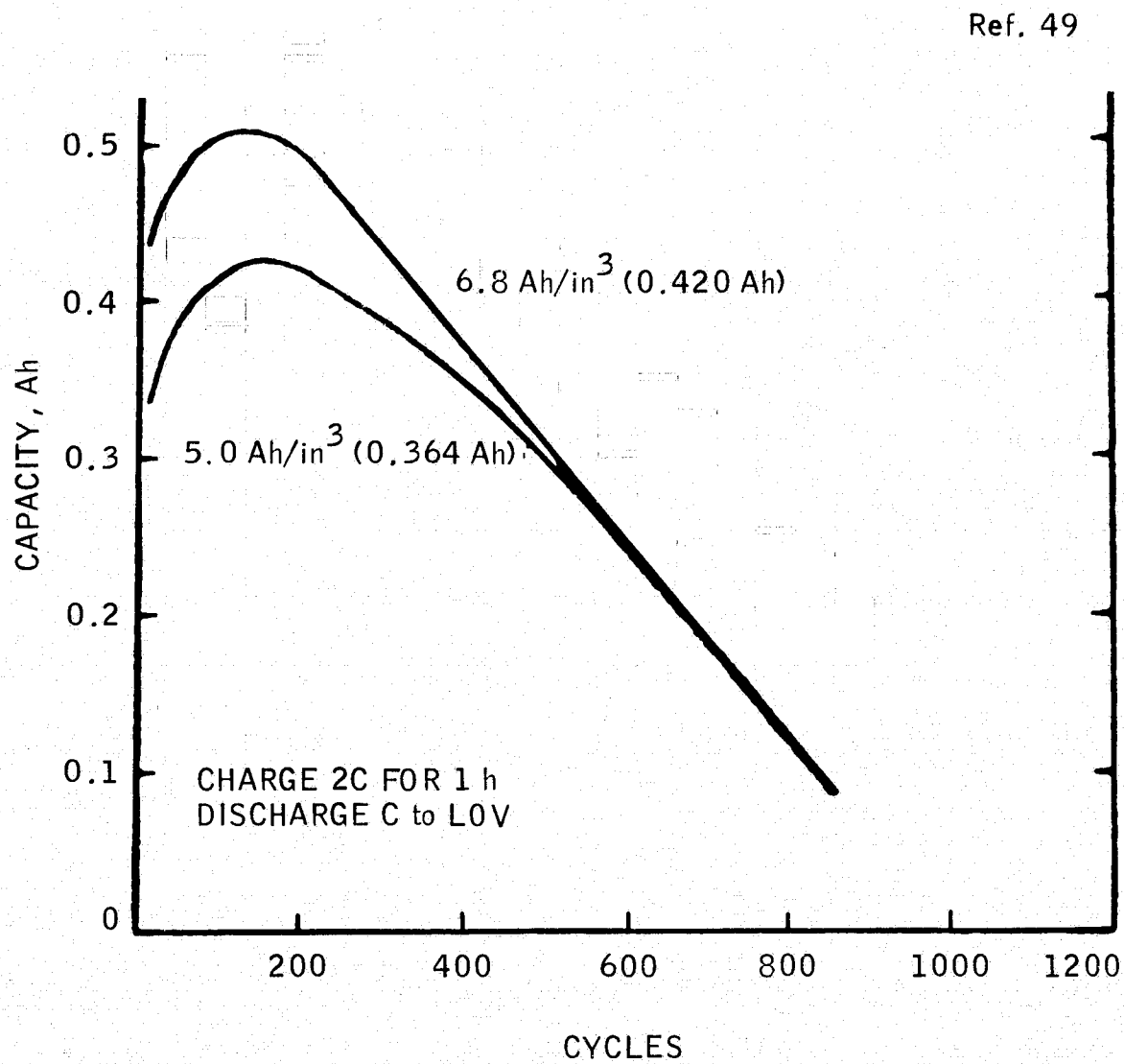


Figure 4-3: Effect of Loading on Nickel Electrode Cycle Life at 110°F

Ref. 49

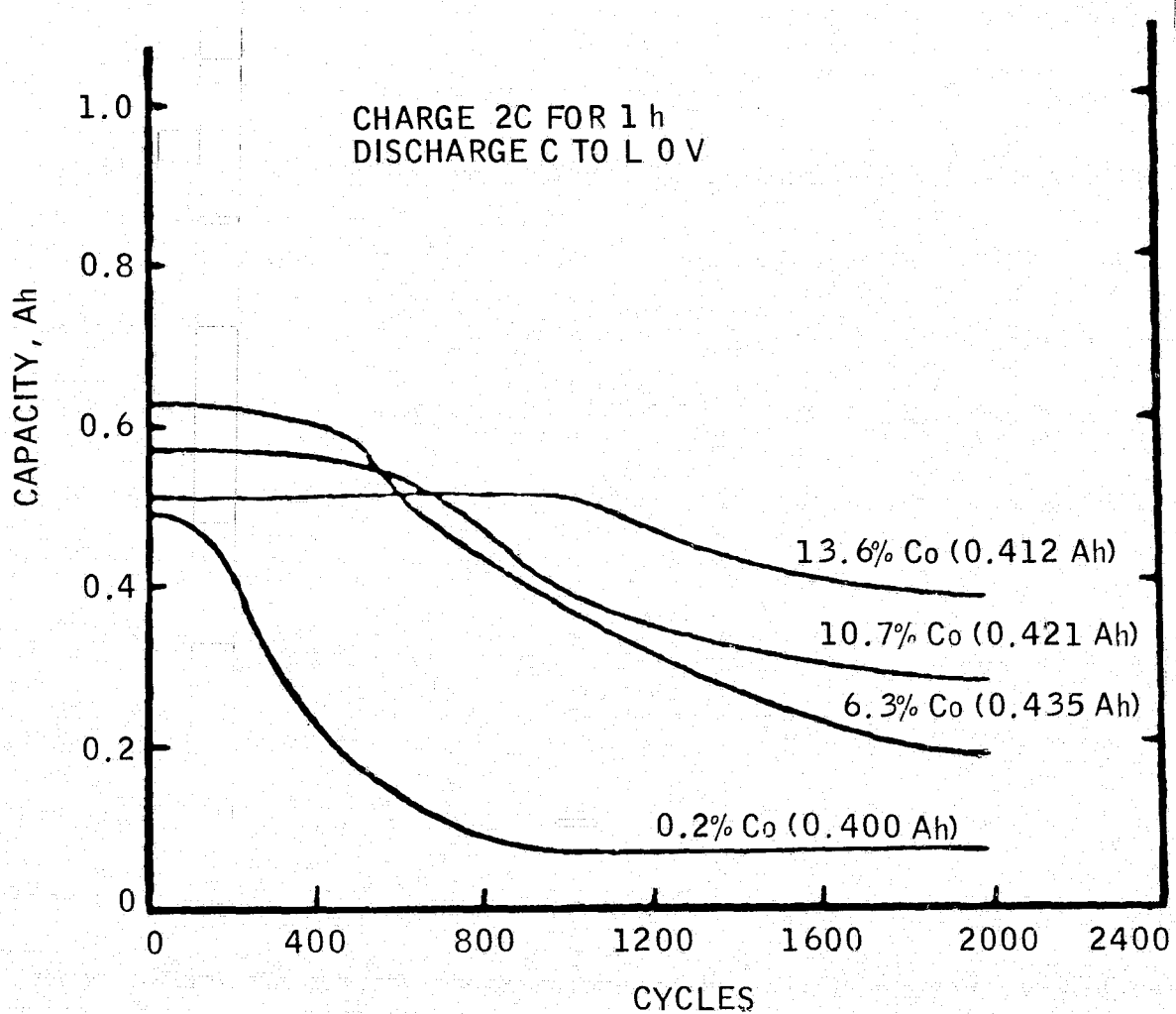


Figure 4-4: Effect of Cobalt Concentration of Nickel Electrode  
Cycle Life at 75°F

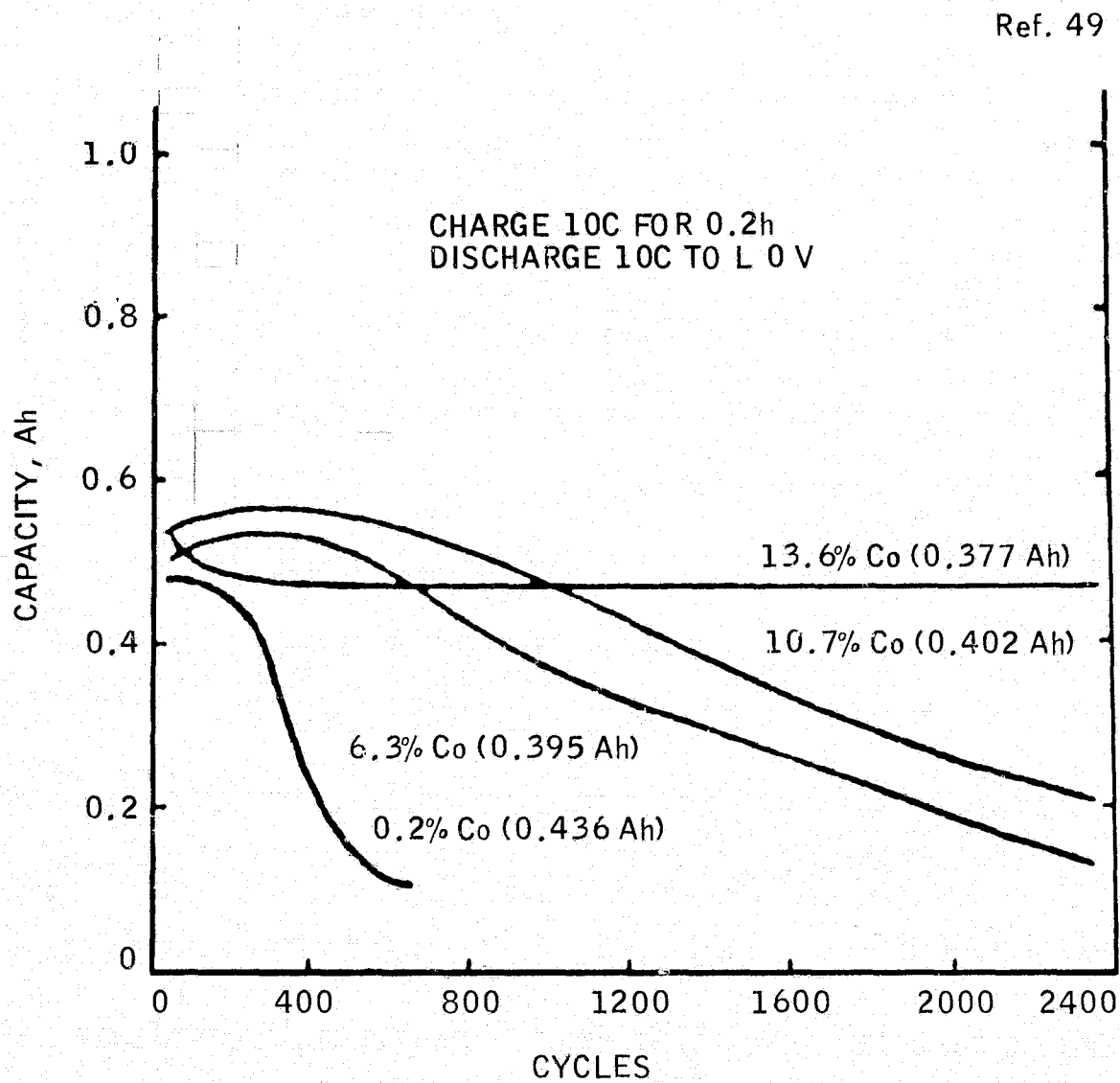


Figure 4-5: Effect of Cobalt Concentration on Nickel Electrode Cycle Life at High Rate and 75°F

Ref. 49

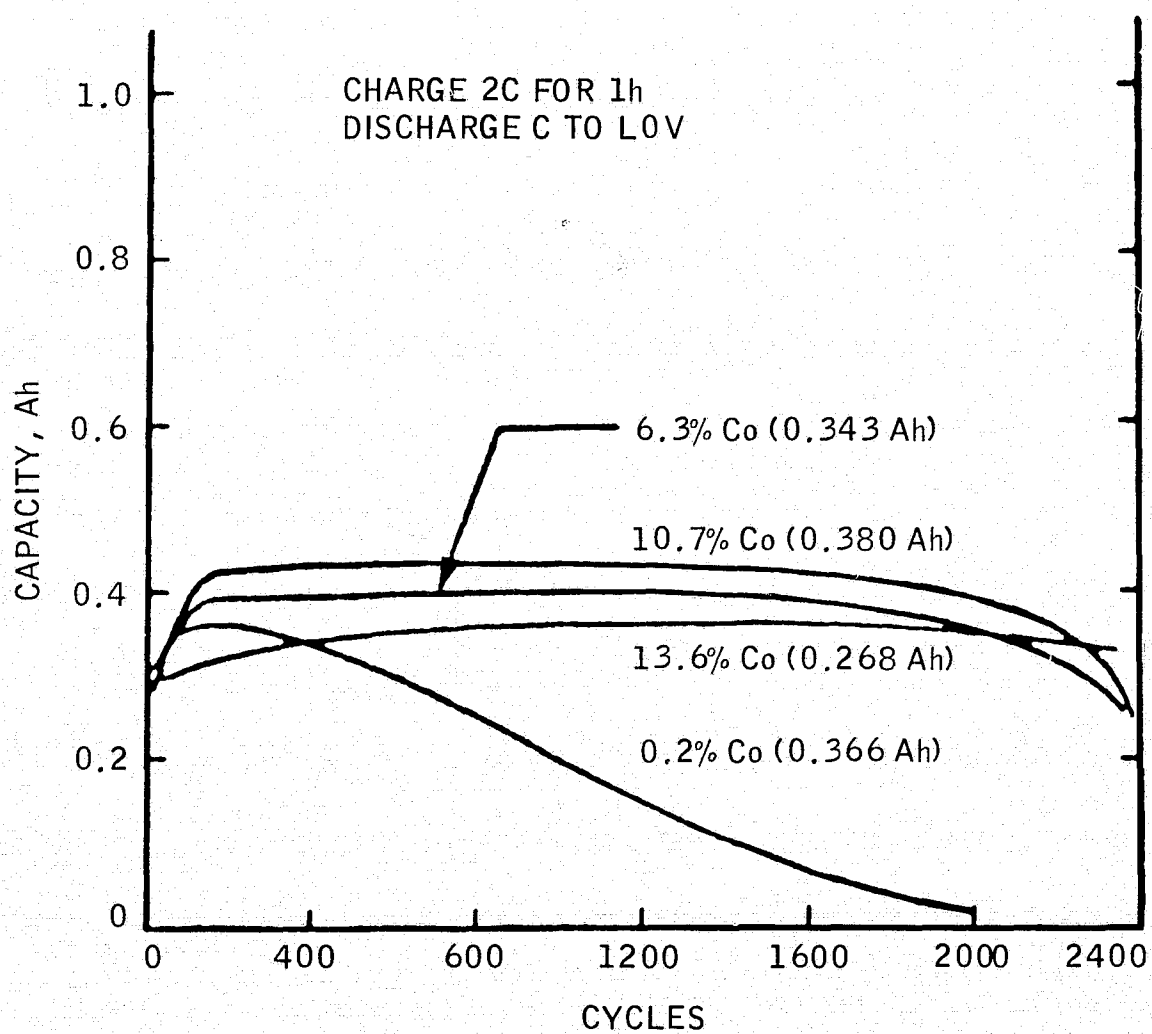


Figure 4-6: Effect of Cobalt Concentration on Nickel Electrode Cycle Life at 110°F

Ref. 49

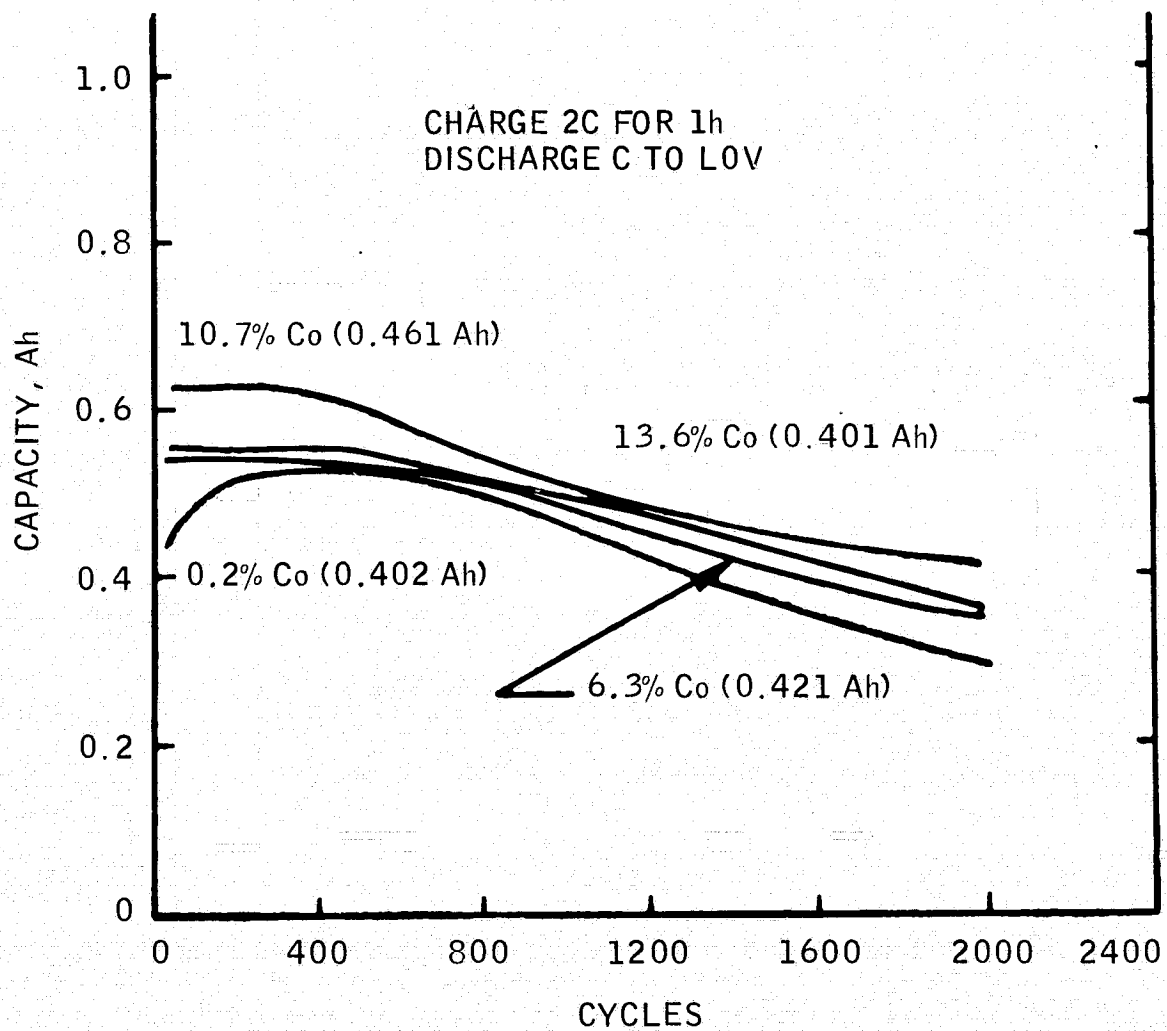


Figure 4-7: Effect of Cobalt Concentration on Nickel Electrode Cycle Life at 20°F



Table 4:1: ELECTROCHEMICALLY IMPREGNATED NICKEL ELECTRODES USED BY  
BEAUCHAMP AND MAURER FOR TESTS ON ADDITIVES

<u>Solution Additive, M</u>	<u>Additive Weight %</u>	<u>Positive Material Capacity Ah/in<sup>3</sup></u>	<u>Utilization %</u>	<u>Surface Area, m<sup>2</sup>/g</u>
None	0.191	6.65	108	88.1
0.1 Co(NO <sub>3</sub> ) <sub>2</sub>	6.26	5.94	117	46.3
0.2 Co(NO <sub>3</sub> ) <sub>2</sub>	10.7	5.95	122	24.8
0.4 Co(NO <sub>3</sub> ) <sub>2</sub>	13.6	5.57	122	24.2
0.1 Cd(NO <sub>3</sub> ) <sub>2</sub>	5.02	6.36	92	-
0.2 Cd(NO <sub>2</sub> ) <sub>2</sub>	6.86	5.80	105	-
0.4 Cd(NO <sub>3</sub> ) <sub>2</sub>	8.44	5.90	109	-

Raw sintered plaque contains 0.032% Co

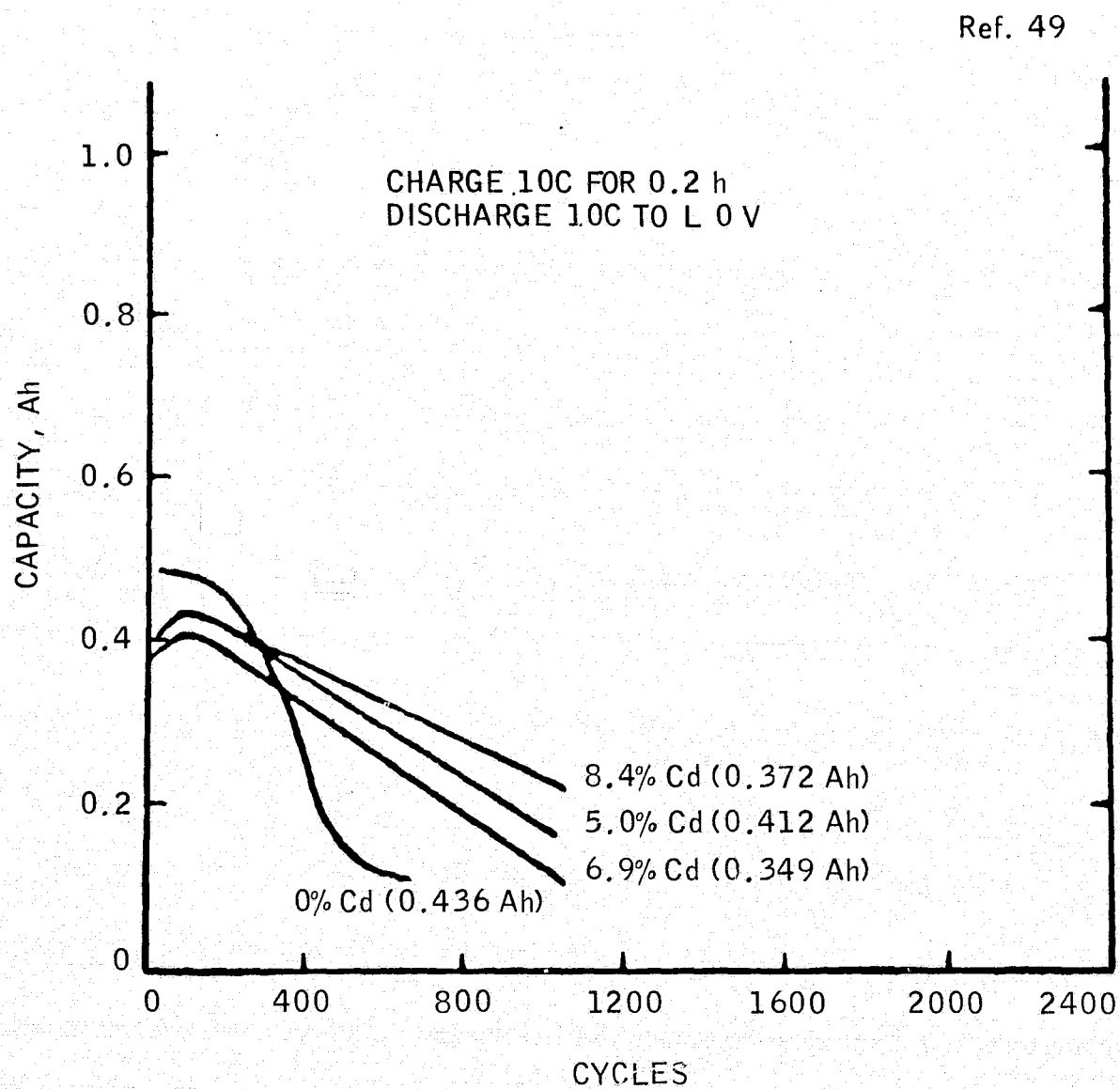


Figure 4-8: Effect of Cadmium Concentration on Nickel Electrode Cycle Life at High Rate and 75°F

Pickett (18) tested nickel electrodes with 2.5% cadmium plus 7.5% cobalt (Tables 4-2 and 4-3). These electrodes had higher active material utilization (118%) than electrodes with 10% cobalt (104%).

In conclusion, cadmium is not as effective as cobalt in reducing capacity fading with cycling. There is some evidence, however, that the combination of cadmium and cobalt may be better than either additive separately.

#### Other Additives

Weininger (44) found that zinc was an effective additive to the nickel electrode, increasing charge acceptance and reducing the rate of capacity fading on cycling. The effects such zinc additions would have on the adjacent cadmium electrode were not determined, however. He also found that the addition of aluminum had a small benefit.

Pickett (18) tested the effects of manganese additions (Tables 4-2 and 4-3), and found that this gave lower utilization of active material than did cobalt. However, less electrode thickening was obtained by the use of manganese.

Lithium hydroxide (1% by weight) was added to KOH electrolyte in cells made at Spectrolab (32). These electrochemically impregnated cells had approximately 9% cobalt hydroxide in the nickel electrode. The cells exhibited lower voltages initially than did cells without lithium. In tests at Yardney (7) the addition of lithium increased capacity 5%; no voltage data were reported, however.

Teflonated cadmium electrodes were reported (32) to have lower utilization of active material than nonteflonated electrodes, and thus reduced their capacity. This conclusion warrants reexamination because the process for making electrochemically impregnated cadmium electrodes had not been fully mature when that

Table 4-2: LOADING CHARACTERISTICS OF NICKEL HYDROXIDE ELECTRODES  
 IMPREGNATED FROM ETHANOL SOLUTIONS WITH  
 VARIOUS ADDITIVES PRESENT

Ref. 18

Plaque Number	Wt. After Impreg. (grams)	Wt. of Deposit (grams)	Thickness Before (inches)	Thickness Increase (mils)	Grams of Deposit per CC of Void	Molarity of Metal Ions in Impreg. Soln.
9A-30	16.733	7.448	0.0306	1.8	2.11	1.8 Ni <sup>++</sup> , 0.2 Mn <sup>++</sup>
10A-30	16.221	7.019	0.0301	1.5	2.03	1.8 Ni <sup>++</sup> , 0.1 Mn <sup>++</sup> , 0.1 Co <sup>++</sup>
11A-30	16.294	7.104	0.0313	1.9	1.97	1.8 Ni <sup>++</sup> , 0.05 Mn <sup>++</sup> , 0.15 Co <sup>++</sup>
12A-30	16.218	7.124	0.0317	1.3	1.95	1.8 Ni <sup>++</sup> , 0.05 Cd <sup>++</sup> , 0.15 Co <sup>++</sup>
13A-30	17.211	8.217	0.0305	4.1	2.15	3.5 Ni <sup>++</sup> , 0.2 Co <sup>++</sup>

Table 4-3: PERFORMANCE OF NICKEL HYDROXIDE ELECTRODES  
IMPREGNATED FROM ETHANOL SOLUTIONS WITH  
VARIOUS ADDITIVES PRESENT

REF. 18

<u>Molarity of Metal Ions in Impreg. Soln.</u>	<u>Plaque Number</u>	<u>Theo.<sup>1</sup> Capacity (A-H)</u>	<u>Measured<sup>2</sup> Capacity (A-H)</u>	<u>% Util.<sup>3</sup> of Active Material</u>	<u>A-H<sup>4</sup> Per In<sup>3</sup></u>	<u>A-H<sup>5</sup> Per Lb.</u>	<u>Thickness<sup>6</sup> Gain (Mils)</u>	<u>Number of Cycles</u>
(30 mil plaque, Mfg. B)								
1.8 Ni <sup>++</sup> , 0.2 Mn <sup>++</sup>	9A-30	1.937	1.700	87.8	6.20	41.6	1.7	34
1.8 Ni <sup>++</sup> , 0.1 Mn <sup>++</sup> , 0.1 Co <sup>++</sup>	10A-30	1.826	1.860	102	6.85	52.0	2.2	35
1.8 Ni <sup>++</sup> , 0.05 Mn <sup>++</sup> , 0.15 Co <sup>++</sup>	11A-30	1.848	1.870	101	6.66	52.1	4.5	38
1.8 Ni <sup>++</sup> , 0.05 Cd <sup>++</sup> , 0.15 Co <sup>++</sup>	12A-30	1.853	2.180	118	8.18	61.0	4.1	37
3.5 Ni <sup>++</sup> , 0.2 Co <sup>++</sup>	13A-30	2.137	2.233	104	7.42	58.9	5.3	35

1 - Value given assumes weight gain of plaque is due to 90% Ni(OH)<sub>2</sub> and 10% additive hydroxide. Additive is not considered active material.

2 - Capacity taken to 0.9 volt cut off versus a Cd bar electrode.

3 - Value assuming only a one electron change occurs.

4 - Value given neglects coined area.

5 - Based on electrode weight prior to charge-discharge cycling.

6 - Increase is difference between original plaque thickness and thickness after number of cycles shown.

study was made.

Indium and antimony have been found to be useful additives to the cadmium electrode in conventional impregnating processes. No information is reported on these additives for the electrochemical impregnation process, however.

## 5.0 CONCLUSIONS AND RECOMMENDATIONS

1. The electrochemical impregnation method has these major features that result in better plates than other methods:
  - (1) The active hydroxide material is deposited directly on the metallic walls of the pores surrounding the nickel skeleton without plugging up the pores.
  - (2) Active material is precipitated first deep inside the electrode, then progresses toward the outside. The interior is filled most densely, with the pores becoming more open toward the surface and hardly any active material deposited on the external surface. Diffusion and conducting mechanisms are facilitated.
  - (3) Well-defined porous, high surface area structures result for both electrodes with microcrystalline within the cadmium electrode and a nickel electrode that under SEM is either channeled and sponge-like or having a petal-like outgrowth.
  - (4) Corrosion can be controlled to negligible amounts permitting use of high porosity plaques without loss of strength.
  - (5) Loading can be high without concomitant thickening of the electrodes. Longer life is expected by minimizing thickening, which is a major cause of electrode degradation.
2. The available evidence shows that electrochemically impregnated nickel and cadmium electrodes are superior to conventional electrodes made by the vacuum immersion impregnation method. There is evidence that the structure of electrochemically impregnated electrodes is the cause of this superiority, but this has never been rigorously demonstrated. One of the important reasons why electrochemically impregnated electrodes are better is that the loading method is a very sensitive one, requiring close control of operating conditions and demanding careful quality control. Evaluation tests should be run on cells

produced by the electrochemical impregnation process, and side-by-side comparisons made with conventional cells.

3. Nickel electrodes made by the electrochemical impregnation process have reached efficiencies of 140%, based on a theoretical one electron transfer. Such unusually high efficiencies have not been obtained by conventional impregnation methods, and the implication is that the efficiency might be elevated even higher with further work. Additional work should be directed toward understanding why such high efficiencies are possible and to learn how to obtain high efficiencies reproducibly.
4. Cadmium electrodes made by the electrochemical impregnation process have reached efficiencies of 94%. Such unusually high efficiencies have not been obtained by conventional impregnation methods. Additional work should be directed toward learning why such high efficiencies are possible and to apply this knowledge in developing superior cadmium electrodes.
5. In attempting to compare electrodes made by electrochemical impregnation with those made by other methods, it became evident that no recognized tests were available to characterize and compare electrodes. Such tests, if available, could also be used to monitor manufacturing processes. Efforts should be made to develop some useful methods; the most worthwhile of these would ultimately become standards in the industry.
6. Review of data by a number of different workers has shown that data was often not in a suitable form or units to permit good comparisons or to make good evaluations of results. For example, loading expressed as grams per cc of void has much merit but often is not available. Even when it is available, the loading information sometimes fails to distinguish between weight gain



and geometry initially vs. after formation and cleaning. An attempt should be made to define information standards for nickel cadmium cell technology. Table 1.1 gives one possible data format.

7. Nickel electrodes made by the electrochemical impregnation method degrade with cycling, though the indications are that the rate of degradation is less than for other methods. The fundamental reasons why degradation occurs is not known, nor is it known why cobalt and other additives extend cycling life. Further work should be done to understand the degradation phenomena in order to learn how better, longer-lived electrodes can be made.
8. Basic physical data on the effects of additives on the nickel electrode are not available and no proven explanation has been given for the observed effects. One possible explanation for the improvement obtained by cobalt additions is a more favorable volumetric expansion, either chemical or thermal. Basic research should be done to understand why additives do or do not help. Electrodeposition tests using a spiral contractometer are suggested as one means to investigate this phenomenon, measuring stresses during charge and discharge.
9. A small amount of test data suggest that the effect of cadmium and cobalt additives together are more effective than either one alone. Well controlled investigations should be made to determine if, in fact, such combinations are of benefit, and what disadvantages, if any, come from such additions.
10. Addition of nickel hydroxide to the cadmium electrode is apparently worthwhile, based on the information given in D180-19046-2. Since plaque corrosion is avoided in electrochemical impregnation, very little nickel hydroxide is produced compared with the conventional vacuum immersion impregnation method. Test information is therefore needed on the effects varying amounts of nickel hydroxide have on the cadmium electrode.

11. Active material is lost from the nickel electrode during formation cycling. Typically, this is about 10%. More information is needed on this phenomenon, especially its cause and reproducibility.
12. Teflonated electrochemically impregnated cadmium electrodes were reported to have lower utilization of active material than nonteflonated electrodes and thus reduced their capacity. This conclusion warrants reexamination because the process for making electrochemically impregnated cadmium electrodes had not been fully mature when that study was made and also because teflonation has proven to be a worthwhile process for vacuum immersion impregnated electrodes.
13. Much of the available data on electrochemical impregnation have been taken at little better than beaker level operations. The data often have considerable scatter, raising questions on some of the apparent conclusions. Also, differences are expected between these beaker-level results and those obtainable under larger scale methods. Efforts should be made to obtain data from production-sized operations.
14. Understanding is inadequate of precisely why high loading results in blisters and electrode expansion. These problems define the practical upper loading level. High energy density designs will use loading levels that approach being marginal with respect to these problems. Therefore, to minimize electrode degradation and to improve energy density, it is worthwhile to understand this phenomena and relate it to electrode manufacturing variables.
15. Major differences are observed in scanning electron micrographs (SEM) of nickel electrodes made by different variations of the electrochemical impregnation method. Important differences would also be expected in maximum energy density, electrical performance and operating life. Investigations are needed to understand the causes and effects of these differences.

16. Studies to make comparisons between different designs or manufacturing methods can be misleading because of the high sensitivity to plaque structure and impregnation parameters. When tests are conducted to determine the effects of variables, it is important that in each case the optimum design is compared. For example, Holleck showed that chemical impregnation is better than electrochemical methods, because his electrochemical design was not an optimum one. Also, Picket showed that optimization conditions for 75% porous plaque cannot be extended to an 82% porous plaque. It is recommended that comparisons be made only in cases where optimum designs are being compared.
17. Capacity of the nickel electrode in the semi-starved condition is less than when flooded. The available data suggest that this difference may be greater for electrochemically impregnated positive electrodes than for conventional processes. No information on this subject is available on the negative electrode. Data and information are needed on this phenomena, especially its cause and reproducibility.
18. Hardman has succeeded in obtaining high energy density in thick electrodes with his electrochemical impregnation method. The fact that his approach is much different than those of other investigators and the fact that he has succeeded are good reasons to follow up on this work. It is recommended that a determination be made of the relevancy of this technology to aerospace applications.
19. Much of the reported electrochemical impregnation work done was in attempts to develop good processes. In most cases there was sufficient success to show improvement in technology and to obtain patents. Generally, however, the investigators did not attain a high enough level of success that they could embark on refinements, examine the effects of design variables, or even obtain a modicum of performance data. Thus, with a few important exceptions, electrochemical impregnation is not a mature technology. Additional work should be done to collect and evaluate information on electrochemical impregnation obtained

on production facilities, rather than laboratory work. Effects of design variables should be emphasized.

20. Nickel electrode capacity increase with cycling is a common characteristic with some electrochemical impregnation methods. This presents a number of problems, such as cell capacity matching and maintenance of the desired negative-positive ratio. Also, in order to properly set precharge, it is important to know whether this capacity increase is initially in the cell in the charged or discharged state. Further work needs to be done on this problem.
21. Although published information does not show the technology of electrochemically impregnated nickel cadmium cells to be in a ready state, proprietary development of this technology is known to be well advanced. Unless cells and electrodes are purchased and tested, this technology cannot be evaluated. Such test and evaluation programs also help provide the support needed to bring the technology to a state of readiness. It is therefore recommended that electrodes and cells be purchased and evaluated. If possible, Motorola cells should be included.
22. As cells made by the electrochemical impregnation process become more available, the need will be more pressing to have available test methods to properly evaluate and compare them with conventional cells. The problem becomes more complicated when it is recognized that the plate loadings, cell size and energy density of such cells are likely to differ significantly from conventional cells on which data may already be available. The need for comparative and accelerated tests should be anticipated and prepared for. Tests currently being used for cell evaluation or acceleration of wearout should be studied and compared and conclusions drawn on the best available test approach.

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