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TECHNICAL REPORT ECOM-2559

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THE EFFECT OF CARBONATED ELECTROLYTE ON THE
PERFORMANCE OF SINTERED PLATE NICKEL-CADMIUM CELLS

BY

PAUL J. RAPPAPORT

FEBRUARY 1965

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UNITED STATES ARMY ELECTRONICS COMMAND · FORT MONMOUTH, N.J.

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PERFORMANCE OF SINTERED PLATE NICKEL-CADMIUM CELLS

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February 1965

DA Task 1C0 14501 A 34A-00

UNITED STATES ARMY ELECTRONICS LABORATORIES

UNITED STATES ARMY ELECTRONICS COMMAND

FORT MONMOUTH, N.J.

Abstract

The effect on the capacities of positive and negative limiting sintered plate Ni-Cd cells of varying the KOH/K₂CO₃ ratio of an electrolyte which is approximately 7N in total alkalinity is reported. K₂CO₃ contents of 24, 71 and 238 g/l were investigated. Data are also presented on the specific resistance of various KOH-K₂CO₃ solutions over the temperature range of 86°F. to -40°F. There was no marked difference in performance of either positive or negative capacity limiting cells with electrolyte containing 24 or 71 g/l of K₂CO₃. However, there was an appreciable adverse effect on the performance of cells when the carbonate content was 238 g/l K₂CO₃, particularly for the negative capacity limiting cells. From the results of the capacity and specific resistance measurements, it is recommended that the maximum allowable carbonate content for the electrolyte in sintered plate Ni-Cd cells be set at 100 g/l K₂CO₃.

CONTENTS

	<u>Page</u>
ABSTRACT	
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	1
Cell Performance Characteristics	1
Resistivity Measurements	2
RESULTS	3
Cell Performance Characteristics	3
Resistivity Measurements	4
CONCLUSIONS	4
REFERENCES	4

FIGURES

1. Summary of Cell Performance Characteristics	5
2. Resistivity of Aqueous KOH-K ₂ CO ₃ Solutions	6

TABLES

I. Summary of Positive Plate Limiting Cell Performance Characteristics	7
II. Summary of Negative Plate Limiting Cell Performance Characteristics	8

THE EFFECT OF CARBONATED ELECTROLYTE ON THE PERFORMANCE OF SINTERED PLATE NICKEL-CADMIUM CELLS

INTRODUCTION

Sintered plate nickel-cadmium cells and batteries have been developed for use with military equipments primarily because of their excellent high rate and low temperature performance. However, it is known that the high rate and low temperature performance is adversely affected as the carbonate content of the initial 31% KOH electrolyte increases. This increase during use of the battery is due mainly to three factors: (1) Absorption of CO_2 from the air (2) Presence of residual carbonate in the positive and negative plates due to insufficient washing during their preparation, and (3) Gradual oxidation of organic separator materials to carbonate. Opinions differ as to how high the carbonate content of the electrolyte may go before it should be changed. Vinal¹ states that some users place the limit at 30 grams K_2CO_3 /liter, whereas others permit as high as 90 grams K_2CO_3 /liter. Casey 2,3 found that the negative sintered plate was more adversely affected than the positive plate by carbonate contamination of the electrolyte and that the negative plates showed a minimum in performance at 20-30 equivalent % of carbonate at 0 and -40°F with a gradual rise to a maximum at about 60 equivalent % followed by a sharp dropoff above this concentration. In order to establish a maximum allowable limit for military sintered plate Ni-Cd cells, an investigation was initiated to study the effect of increases in the carbonate content of the electrolyte on the capacity of these cells and on the specific resistance of the electrolyte.

EXPERIMENTAL PROCEDURE

Cell Performance Characteristics

Each test cell consisted of three sintered plates which were assembled in Bakelite C-11 containers and mechanically separated by grooved supports. Both positive capacity limiting and negative capacity limiting cells were used in order to determine the effect of the various carbonated electrolytes on each plate separately. The positive limiting cells contained two negative plates and one positive plate and the negative limiting cells contained two positive plates and one negative plate. All plates were 3-5/16" high x 2-7/8" wide with the negative plates having a thickness of .037" and the positive plates a thickness of .044". A sintered cadmium plate was used as a reference electrode in each cell so that both positive and negative plate capacities could be determined.

Three electrolytes were used in this phase of the investigation. They were prepared by mixing approximately 7N aqueous solutions of available reagent grade KOH and K_2CO_3 . The first solution, designated as Electrolyte 1, was a solution of KOH with no deliberate addition of K_2CO_3 . Electrolytes 2 and 3 had higher carbonate concentrations as a result of adding K_2CO_3 to Electrolyte 1. The amounts of KOH and K_2CO_3 in the three electrolytes were determined by titration with

standard H_2SO_4 to phenolphthalein and screened methyl orange end points and were found to be as shown at the bottom of Tables I and II. It can be seen that Electrolyte 1, which was intended to be pure KOH, actually had almost 24 g K_2CO_3 /l. Most of this carbonate came from the KOH pellets used to prepare the solution and some of it from the distilled water used.

A total of twelve test cells were assembled, two positive capacity limiting and two negative capacity limiting for each of the three electrolyte concentrations. All twelve cells were first filled with Electrolyte 1 (38.1 g/l KOH + 23.8 g/l K_2CO_3) to determine their initial capacities at approximately the five hour rate (0.5A) at 70°F. After three of these cycles the electrolyte was changed in eight of the cells to the other two concentrations under investigation and the rest of the electrical tests were then carried out on all twelve cells. All discharges were carried out at 0.5 A, except for one discharge at 7.5 A. This rate was chosen to represent a high rate discharge since USAKI specifications require 15 minutes of service to a cutoff voltage of 1.0 V/ cell when Ni-Cd cells are discharged at three times the rated capacity in amperes. In this case considering the average capacity of the cells to be 2.5 A. H. at the five hour rate this would be 3×2.5 or 7.5 A. All charges were conducted at 0.5 A. for eight hours or a total input of 4 A.H. (160% of the average capacity of 2.5 A.H.). Charges were also carried out at -40°F. and -65°F because it had been found in the past that low temperature charging of Ni-Cd cells sometimes improves their subsequent discharge performance at low temperatures.

Resistivity Measurements

Resistivity determinations were conducted on five solutions having a total alkalinity of approximately 7N and varying from almost pure KOH to pure K_2CO_3 . The exact concentrations of the five solutions were again determined by titration with standard H_2SO_4 to the phenolphthalein and screened methyl orange end points. These concentrations are given in Figure 2. Solutions A and C are the same as Electrolytes 1 and 3 used in the cell performance studies. The measurements were made at intervals of 18°F (10°C.) from 86°F. (30°C.) down to -40°F. (-40°C.). In those cases where the solution froze above -40°F. the measurements were made to the selected temperature closest to freezing.

A conductivity bridge, RC16B2, made by Industrial Instruments, Inc., and a glass fill type conductivity cell with two platinized electrodes a fixed distance apart were used for the measurements. The cell constant K was determined using a standard solution of H_2SO_4 whose specific conductance L was known.

K was obtained from the following formula:

$$K = L \times R_m$$

where

K = Cell constant in cm^{-1}

L = Specific conductance of standard H_2SO_4 in $\text{ohm}^{-1}\text{cm}^{-1}$

R_m = Measured resistance in ohms

The specific resistance or resistivity of the various solutions was determined from the following formula:

$$R = \frac{R_m}{K}$$

where

R = Specific resistance in ohm-cm

All low temperature measurements were made by cooling the solution below the desired temperature with a dry ice in alcohol bath and then allowing the solution to warm to the specified temperature.

RESULTS

Cell Performance Characteristics

The results obtained on the electrical tests of the cells are shown in Tables I and II and also in Figure 1. In Tables I and II the results are given for both cells at each test condition in terms of the actual capacity and in terms of the percentage of the initial capacity obtained with each cell when it was discharged at 0.5 A. at 70°F . in Electrolyte 1. In Figure 1 the average values for the two cells at each test condition are plotted as the percentage of the initial capacity.

The results show that the negative limiting cells were more adversely affected than the positive limiting cells as the carbonate content of the electrolyte was increased. With the positive limiting cells the highest carbonate content electrolyte gave significantly poorer results than the other electrolytes only at -65°F . In the case of the negative limiting cells poorer performance was obtained with the highest carbonate electrolyte at the high discharge rate (7.5 A.) at 70°F . and also at -40°F and -65°F . It is significant to note that in all cells, both positive limiting and negative limiting, there was no appreciable difference in performance between cells containing Electrolyte 1 (24 g/l K_2CO_3) and those containing Electrolyte 2 (11 g/l K_2CO_3). The only noticeable effect of the low temperature charging is that the performance of the positive limiting cells appears to be lower when charged and discharged at -65°F . than when charged at 70°F . and discharged at -65°F . The reason for this is not known. This effect does not show up with the positive limiting cells at -40°F . nor with the negative limiting cells at either -65°F . or -40°F .

Resistivity Measurements

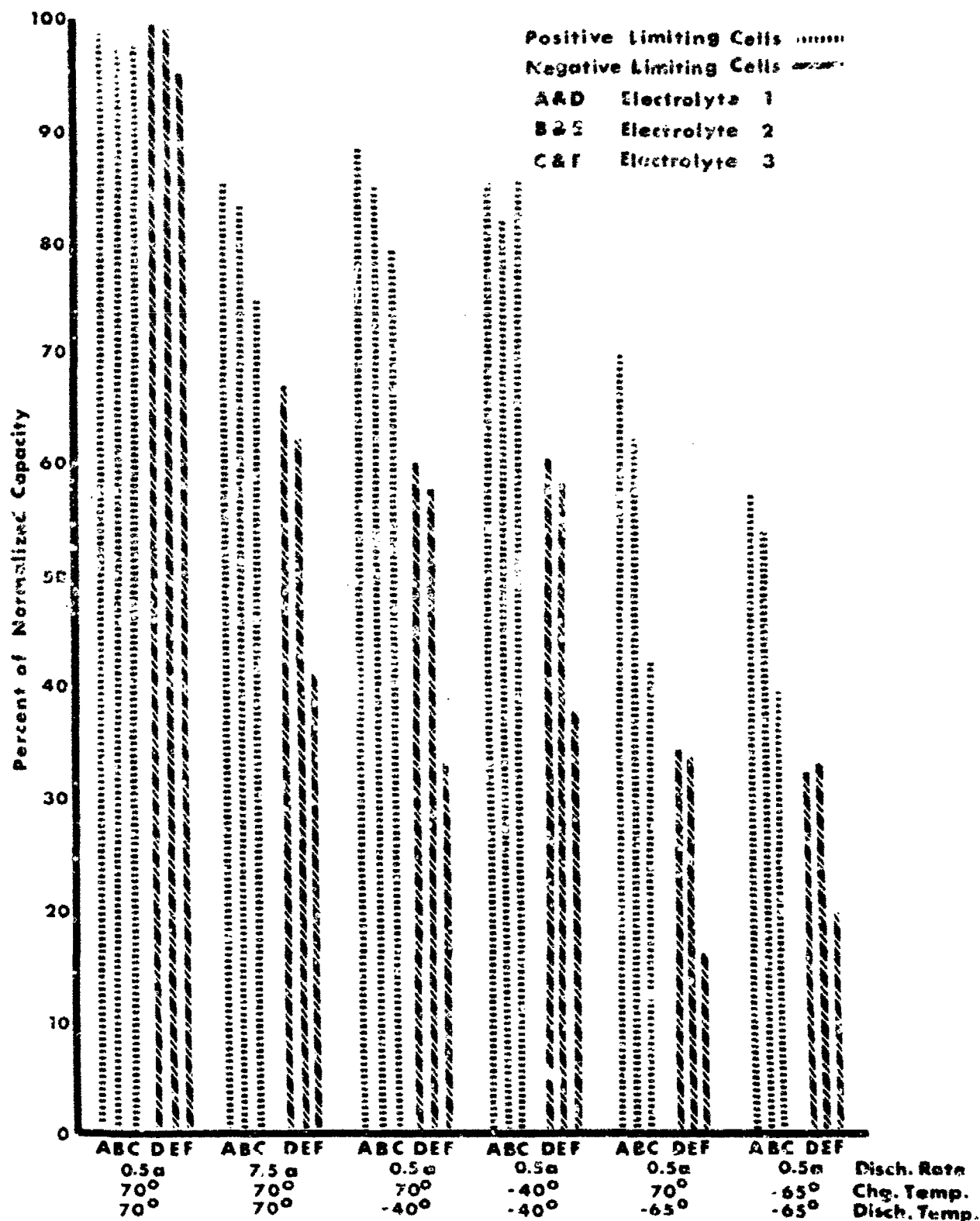
The results of the resistivity measurements are shown in Figure 2. The resistivities are plotted in ohm-cms. against temperature in °F. and °C. for the five solutions whose concentrations are indicated in the figure. It can be seen that at any temperature the resistivity of the solutions increased as the carbonate content increased and for all solutions the resistivity increased as the temperature decreased. All solutions tested except that with the lowest carbonate content (24 g/l) froze above -40°F. This indicates that to prevent freezing of the electrolyte at -40°F., the carbonate content must be less than 127 g/l K_2CO_3 .

CONCLUSIONS

From the results of the cell performance tests it can be concluded that the maximum allowable carbonate content of the electrolyte lies between 71 and 238 g/l K_2CO_3 . Furthermore, if performance down to -40°F is required, then the carbonate content of the electrolyte should be below 127 g/l K_2CO_3 in order to prevent freezing at -40°F. It is therefore recommended that the maximum allowable carbonate content for the electrolyte in sintered plate Ni-Cd cells be set at 100 g/l K_2CO_3 .

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2. E. J. Casey and P. E. George, "The Electrical Output of Sintered Plates of Nickel-Cadmium Batteries I", DRCL Report No. 156, March, 1954.
3. E. J. Casey and P. E. Lake, "Sintered Plates of Nickel-Cadmium Batteries II, Extent of Effects of Carbonate Contamination on Electrical Output", DRCL Report No. 186, April, 1955.



SUMMARY OF CELL PERFORMANCE CHARACTERISTICS

FIG. 1

°F 36
68
100
140
180
220
260
300

°C 30
20
10
0
-10
-20
-30
-40

A B C D E

RESISTIVITY OF AQUEOUS KOH-K₂CO₃ SOLUTIONS

Electrolyte Composition				
Sol'n	N	KOH g/l	N	K ₂ CO ₃ g/l
A	6.80	381	.34	23.8
B	5.34	301	1.84	127
C	3.56	201	3.44	238
D	1.78	100	5.30	366
E	0	0	7.29	504

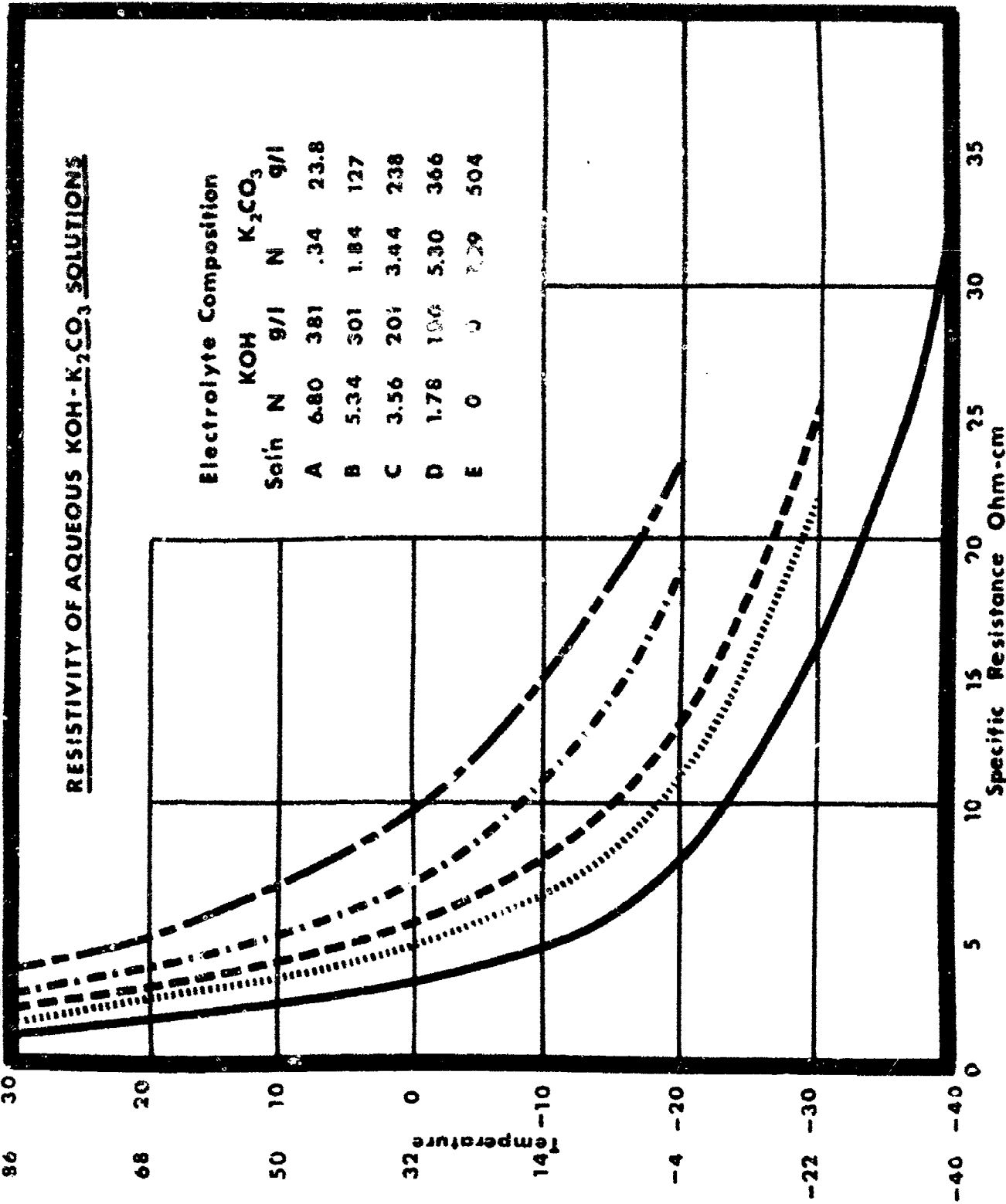


FIG. 2

TABLE II

SUMMARY OF NEGATIVE PLATE LIMITING CELL PERFORMANCE CHARACTERISTICS

Electrolyte	Cell No.	Charge Temp.	* 70°F	70°F	70°F	70°F	-40°F	70°F	-65°F
		Dischg. Temp.	70°F	70°F	70°F	70°F	-40°F	-65°F	-65°F
		Rate	0.5 A	0.5 A	7.5 A	0.5 A	0.5 A	0.5 A	0.5 A
Electrolyte 1	7	Capacity (A.H.) %	3.08 100	----- -----	2.00 64.9	1.79 58.1	1.86 60.4	1.03 33.4	1.11 36.0
	8	Capacity (A.H.) %	2.65 100	----- -----	1.88 70.0	1.67 63.0	1.61 60.7	0.93 35.1	0.77 29.0
	9	Capacity (A.H.) %	3.08 100	3.06 99.5	2.06 66.9	1.93 62.6	1.86 60.4	1.06 34.4	1.04 33.8
Electrolyte 2	10	Capacity (A.H.) %	2.56 100	2.51 98.0	1.50 58.6	1.36 53.1	1.45 56.6	0.86 33.6	0.84 32.8
	11	Capacity (A.H.) %	2.34 100	2.31 98.9	1.06 45.3	0.92 39.4	0.96 41.0	0.46 19.7	0.55 23.5
Electrolyte 3	12	Capacity (A.H.) %	2.17 100	1.99 91.7	0.81 37.3	0.59 27.2	0.75 34.6	0.29 13.3	0.37 17.0

Electrolyte 1 - 6.8N(381 g/l) KOH - 0.34N(23.8 g/l) K₂CO₃ *All cells on this cycle contained Electrolyte 1 to determine initial capacity.

Electrolyte 2 - 5.7N(320 g/l) KOH - 1.03N(71 g/l) K₂CO₃

Electrolyte 3 - 3.56N(201 g/l) KOH - 3.44N(238 g/l) K₂CO₃

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(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) U. S. Army Electronics Command Fort Monmouth, N. J.		2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP
3. REPORT TITLE THE EFFECT OF CARBONATED ELECTROLYTE ON THE PERFORMANCE OF SINTERED PLATE NICKEL-CADMIUM CELLS		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report		
5. AUTHOR(S) (Last name, first name, initial) Rappaport, Paul J.		
6. REPORT DATE February 1965	7a. TOTAL NO. OF PAGES 8	7b. NO. OF REFS 3
8a. CONTRACT OR GRANT NO. b. PROJECT NO. 100 14501 A 34A c. Task No. -00 d. Subtask No. -02	9a. ORIGINATOR'S REPORT NUMBER(S) ECOM-2559 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nickel-Cadmium Cells						
Sintered Plates						
Potassium Carbonate (K_2CO_3)						
Specific Resistance ($\Omega\text{-cm}$)						
Positive Capacity Limiting Cells						
Negative Capacity Limiting Cells						

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