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FINAL REPORT

for

STUDY OF ADDITIVES TO IMPROVE NICKEL HYDROXIDE ELECTRODE BEHAVIOR

Contract No. NAS 5-3349

W. N. Carson, Jr.

Chemical and Materials Engineering Laboratory

Advanced Technology Laboratories

GENERAL ELECTRIC COMPANY

Schenectady, New York

March 15, 1964

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

GODDARD SPACE FLIGHT CENTER

GREENBELT, MARYLAND

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ABSTRACT

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This report describes the work and results of an investigation on the use of spinel additives to nickel hydroxide electrodes. The objective of the investigation was to determine if one or more of these additives would give nickel hydroxide electrodes with improved reversibility on charge and discharge. With the exception of scandium, no marked effect on reversibility was found, the scandium appears to decrease the overall utilization and is thus unattractive as an additive.

Author

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1.0 INTRODUCTION

Interest in modifying the electrical behavior of the nickel hydroxide electrode used in nickel-cadmium cells comes from the desire to improve these cells for use in space and other premium applications. The use of nickel-cadmium cells in space applications, for which their charge and discharge characteristics, considered by themselves, would not immediately recommend them, depends upon a combination of other factors, which although individually are not unique to the nickel-cadmium cell, do not yet exist in fully proven form in any other cell system. These characteristics are the ability to withstand many thousands of charge-discharge cycles without maintenance and appreciable change in electrical properties while operating in a fully sealed condition and accommodating moderate rates of overcharging. A major difficulty in using the nickel-cadmium cell is the relatively large irreversibility of the cell voltage between charge-discharge in a cell of relatively low operating voltage. This irreversibility is evidenced by the substantial difference in the average voltage levels during charge and discharge at the same current. Studies have shown that most of the irreversibility shown by the cell is associated with the nickel-hydroxide electrode.

A possible means for modifying the behavior of an electrode is the use of an additive which will modify the electrode response. Improved reversibility in an electrode can be obtained by using a catalyst to speed up the limiting reaction involved in the irreversibility; however, in the case of the nickel-hydroxide electrode, no universally accepted theory exists explaining the observed irreversibility. In fact, there is no universally accepted theory on how the electrode charges in the first place.

2.0 TECHNICAL

2.1 Additives

Historically, the use of additives in the nickel-hydroxide electrode, particularly cobalt, is well known. The beneficial aspects for cobalt are better retention of charge and longer cycling life. Little work has been done with additives other than cobalt, so there was little precedent for selecting additives to try in the program. The examination of the little data available indicated that additions of spinels might be helpful in improving electrode performance, and our study was based on the use of this type additive. With respect to improving the voltage reversibility, the spinels are not effective. They may have other beneficial effects, but as of this date, these are not known.

Doran[1] has reported that the addition of magnesium (Mg^{+2}) or

1. R.J. Doran, Paper presented at Third International Battery Symposium, Bournemouth, England; October 1962.

scandium (Sc^{+3}) ions to the nickel hydroxide greatly improves the electrochemical behavior of the electrodes. He claims that the presence of 20 mole per cent scandium hydroxide in the nickel hydroxide used to impregnate the electrode gives a substantial elevation and smoothing of the working potentials; the elevation is greater for discharge than charge. No significant reduction in usable capacity was reported in spite of the fact that scandium is electrochemically inactive and only 80% of the normal quantity of nickel hydroxide was present. The effect of temperature on the doped electrodes was reported as being much less than for the undoped electrodes; the difference between charging and discharging voltages was considerably less for the doped electrodes for all temperatures from -25°C to +50°C, although the improvement shown at -25°C is not large.

Table I, taken from the paper by Doran, shows the reversibility improvement claimed for the scandium-doped electrode. The potential differences between the charge and discharge curves at the 50% charge point are listed.

TABLE I

EFFECT OF SCANDIUM CONTENT ON REVERSIBILITY

Cation % Sc	0	2.5	5	10	15	20	25
Δ V (mv)	130	85	75	65	65	65	65

Our work has only partially confirmed Doran's work, but there is undoubtedly some beneficial effect in adding scandium to the electrode.

The mechanism by which the addition of foreign ions to the electrode active material improves the electrode performance is as yet not resolved. A possible theory is based on the fact that the foreign ions known to improve electrode behavior can form mixed oxides with nickel. These mixed oxides are probably low-temperature spinels, which are known to possess a number of electrical and magnetic properties not shown by the simple oxides. Work in the Advanced Technology Laboratories of the General Electric Company has shown that many spinels are active catalysts for the decomposition of peroxyl ion (HO_2^-) in basic solutions. Peroxyl ion forms at a much lower electrode potential than Ni(III), and can react with nickel (III) to form oxygen:

$$Ni_2O_3 + 2H_2O + HO_2^- \longrightarrow O_2 + 2\,Ni(OH)_2 + OH^-$$

Any interference in the formation of peroxyl ion would be expected to have two effects leading to improved electrode performance:

1. The oxygen evolution reaction mechanism involving interaction of peroxyl and nickel (III) would be disrupted with consequent improvement in current efficiency since current is not used to create the peroxyl ion and the nickel (III) ion reacting with it.

2. The potential of the nickel electrode will rise because the reaction occurring at lower potential is not present. When two simultaneous reactions occur, the electrode potential normally falls between the potential at which each reaction occurs.

The formation of peroxyl ion at an electrode is inhibited by a large activation energy requirement. The formation reaction is autocatalytic, at least for small concentrations of peroxyl ion. The inclusion of an active peroxyl ion decomposition catalyst in the electrode structure, such as a spinel, would block the formation of peroxyl by reducing and keeping the concentration of this ion at a very low value. The observed effect of use of spinels in an electrode should therefore be the elimination of any reactions involving peroxyl ion. This could raise the discharge voltage of the electrode.

If the irreversibility of the nickel-hydroxide electrode is due to a mechanism involving peroxyl ion, the use of spinels in the nickel hydroxide used to impregnate the electrode would be expected to give an improvement in electrode reversibility. No marked effects were found, hence the participation of a peroxyl mechanism is essentially ruled out in the behavior of the nickel-hydroxide electrode on charge or discharge.

2.2 Spinels

Spinels are a group of metal oxides that form crystals in a special crystal lattice characterized by a unit cell containing 32 oxygen atoms in a cubic, close-packed arrangement, with 64 tetrahedral and 32 octahedral sites available for the metal ions, which generally are of two valence types. Normally, the metal ions occupy eight tetrahedral and sixteen octahedral sites; the structure can be normal or inverse depending upon the distribution of the two types of cations between the sites. The number of spinels which can occur is very great, particularly as many of the simpler ones can be mixed to give a wide range of solid solutions. Table II gives a partial list of the spinels which gives an idea of the possibilities using these compounds for electrode additives.

TABLE II

PARTIAL LISTING OF SPINELS

Valence X ion	Valence Y ion	Formula	Examples
1	3	XY_5O_8	$LiFe_5O_8$, $LiAl_5O_8$
1	4	$X_4Y_5O_{12}$	$Li_4Ti_5O_{12}$
1	6	X_2YO_4	Ag_2MoO_4, Na_2WO_4
2	3	XY_2O_4	$MgAl_2O_4$ (Spinel), $FeFe_2O_4$ ("Magnetite"), $ZnFe_2O_4$, and generally the ferrites; chromites, aluminates, gallates, and indates of divalent metals.
2	4	X_2YO_4	Mg_2TiO_4 and other titanates
-	3	X_2O_3	γ - Al_2O_3, γ - Fe_2O_3, and γ - Mn_2O_3

The formation of spinels at low temperatures (below 100°C) is observed for many of the combinations; however, many spinels require firing at elevated temperatures before definite spinel formation is observed. In our experiments, spinels formed in situ were of necessity the low temperature type since heating of the electrode is not possible.

Experimentally, we have tried adding the spinels to the nickel hydroxide in three ways:

A. Adding the nitrate of the ion which could form a spinel with nickel (II) or nickel (III) to the nickel nitrate impregnating solution. The mixed hydroxides are then precipitated in the plaque, and spinel formation, if any, takes place during the subsequent treatment of the electrode.

B. Adding the mixed nitrates of the ions forming the spinel to the nickel nitrate impregnating solution and proceeding as for "A". Here the amount of spinel formed is probably small, but is intimately mixed throughout the electrode.

C. Adding the preformed, fired spinels to the nickel nitrate solution as a suspension of fine powder and trapping the particles in the precipitation step. Here the amount of spinel is large, but may be poorly distributed.

3.0 EXPERIMENTAL

3.1 Materials

The test electrodes were made from unimpregnated sintered-nickel plaques of the BB405 size (1 5/8"x 2 7/8"). These plaques were standard SAFT[1] VO positives, made at General Electric's Gainesville Florida Plant.

The impregnating solutions were made up to a total of 5M metal ion content. The solutions were made from cobalt-free, reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ as follows:

no additives	1460 g/l	$Ni(NO_3)_2 \cdot 6H_2O$
10% "	1310 g/l	"
15% "	1230 g/l	"
20% "	1163 g/l	"

Three milliliters of concentrated (80%) nitric acid per liter of solution were added. The additives studied are listed in Table III. Except as noted below, all chemicals used were reagent grade material obtained from Fisher Scientific Company.

The scandium oxide used was 99.5% pure commercial material from United Mineral and Chemical Corporation. The oxide was dissolved in an excess of hot nitric acid, and the solution evaporated to incipient dryness before adding to the nickel-nitrate. This reduced the free acid level to a low value.

The gallium and indium oxides used were commercial material from Chemical Procurement Laboratories. These required prolonged digestion

1. SAFT is the abbreviation for Societe des Accumulateurs Fixes et de Traction, S.A. Paris France - General Electric manufactures nickel-cadmium cells under a SAFT license. VO is the designation for flat plate cell material; the positive type has 80% porosity.

TABLE III

COMPOSITION OF IMPREGNATION SOLUTIONS

Code	Name	Additive Compound	g/l	Possible Spinel
A	None	—	—	—
B	10Co 20Co	$Co(NO_3)_2 \cdot 6H_2O$ "	146 292	Ni Co_2O_4 "
C	10Sc 15Sc 20Sc	Sc_2O_3 " "	34.5 51.8 69.0	Ni Sc_2O_4 " "
D	10Mg 20Mg	$Mg(NO_3)_2 \cdot 6H_2O$ "	178 256	Mg Ni_2O_4 "
E	10Mn	$Mn(NO_3)_2$ (1)	179	Mn Ni_2O_4
F	10Ce	$Ce(NO_3)_3 \cdot 6H_2O$	154	Ni Ce_2O_4
G	10Fe	$Fe(NO_3)_3 \cdot 9H_2O$	202	Ni Fe_2O_4
H	10Cr	$Cr(NO_3)_3 \cdot 9H_2O$	200	Ni Cr_2O_4
I	10Al 20Al	$Al(NO_3)_3 \cdot 9H_2O$ "	188 376	Ni Al_2O_4 "
J	10Di	$Di(OH)_3$ (2)	95.5	Ni Di_2O_4
K	10In	In_2O_3	69	Ni In_2O_4
L	10Mo 20Mo	$(NH_4)_2MoO_4$ "	89 177	Ni MoO_4 "
M	10VO	$VOSO_4$	100	Ni VO_4
N	10 Y 20 Y	Y_2O_3 "	57 114	NiY_2O_4 "
O	10CoAl 20CoAl	$Co(NO_3)_2 \cdot 6H_2O$+ $Al(NO_3)_3 \cdot 9H_2O$ $Co(NO_3)_2 \cdot 6H_2O$ $Al(NO_3)_3 \cdot 9H_2O$	146 375 292 750	$CoAl_2O_4$ " "
P	10Ag Mo	$AgNO_3$ + $(NH_4)_2MoO_4$	340 89	Ag_2MoO_4

Table III con't

Code	Name	Additive Compound	g/l	Possible Spinel
Q	10CdZr	$Cd(NO_3)_2 \cdot 6H_2O+$ $ZrO(NO_3)_2 \cdot$	616 250	Cd_2ZrO_4
R	10MgAl	$Mg(NO_3)_2 \cdot 6H_2O+$ $Al(NO_3)_3 \cdot 9H_2O$	256 375	$MgAl_2O_4$
	20MgAl	$Mg(NO_3)_2 \cdot 6H_2O+$ $Al(NO_3)_3 \cdot 9H_2O$	512 750	"
S	1 Os	OsO_4	5	none
T	1 Rh	$RhCl_3$	20	none
U	1 Pd	$Pd(NO_3)_2$	50	none
V	1 Pt	$H_2PtCl_6 \cdot 2H_2O$	50	none
W	1 Ru	Ru	10	none
Y	10CuWX(3)	$CuWO_4$	156	$CuWO_4$
Z	10ZnTiX	Zn_2TiO_4	121	Zn_2TiO_4
AA	10CoAlX	$CoAl_2O_4$	89	$CoAl_2O_4$
AB	10Mg AlX	$MgAl_2O_4$	71	$MgAl_2O_4$
AC	10CdZrX	Cd_2ZrO_4	190	Cd_2ZrO_4
AE	10CoCrX	$CoCr_2O_4$	114	$CoCr_2O_4$
AF	10Sc (4)	Sc_2O_3	34.5	$NiSc_2O_4$
AG	15ScR	"	51.8	"
AH	20ScR	"	69.0	"
AI	10Ga	Ga_2O_3	47.0	$NiGa_2O_4$
AJ	1Ir	$IrCl_3$	50	none

(1) Obtained as 50% solution. weight given is solution weight used.
(2) Didymium hydrate, see text for discussion.
(3) Preformed spinels added as fine powders to nickel-nitrate impregnation bath are shown by suffix X.
(4) Reruns are shown by suffix R.

with acid to get into solution, the excess acid was removed as for the scandium before use.

The $Di(OH)_3$ is didymium hydrate, which is a mixture of rare earth hydrates that is left from rare earth ores after removal of cerium and non-rare earth metals. Our sample was from Davison Chemical Company and had the approximate composition, expressed in oxide equivalents, shown in Table IV.

TABLE IV

DIDYMIUM HYDRATE COMPOSITION

(Approximate)

METAL	OXIDE	PER CENT
Lanthanum	La_2O_3	16.9
Cerium	CeO_2	0.5
Praseodymium	Pr_6O_{11}	3.5
Neodymium	Nd_2O_3	12.0
Samarium	Sm_2O_3	2.0
Gadolinium	Gd_2O_3	1.3
Yttrium	Y_2O_3	0.2
Other rare earth's oxides		0.6
Foreign metal Ca, Fe, etc. oxides		2.4

The remainder is made up of combined water to form the hydrates:

$$Di_2O_3 + 3\ H_2O \longrightarrow 2\ Di(OH)_3$$

In use, the hydrate was dissolved in a slight excess of warm, dilute acid and then added to the nickel nitrate solution.

The platinum metal additive starting materials were all obtained from Englehard. The chlorides were boiled repeatedly with nitric acid to remove the bulk of the chloride ion; the ruthenium metal was dissolved in aqua regia and the chloride solution repeatedly boiled with nitric acid. In no case was all of the chloride ion removed below detection level, but the final concentrations were quite low. This removal of chloride was felt necessary to prevent confounding the data with another variable.

The preformed spinels were purchased or made from the corresponding nitrates as described below. The cobalt molybdate was obtained from Chemical Procurement Laboratories, the cupric tungstate and cobalt aluminate were obtained from K and K Laboratories, Inc., and the zinc titanate was supplied by Titanium Alloy Division of National Lead Company. The other preformed spinels tested (i.e. magnesium aluminate, lithium alumino-aluminate, cadmium zirconate, and cobalt chromite) were made by dissolving the correct proportions of the metal nitrates in warm water, and carefully drying the solution to obtain the mixed nitrates. These were then calcined at 400° to 500°C to drive off the nitrogen oxides, ground to -350 mesh, refired in oxygen at 550°C for one hour, and reground to -350 mesh for use. The purchased spinels were also ground to -350 mesh prior to use. The compounds all showed the presence of a spinel lattice in X-ray diffraction tests.

The mercuric oxide-mercury reference electrodes were made using an 8 mm glass tube with a platinum lead. A layer of pure mercury covered this lead; a layer of a mixture of mercury and red mercury oxide was placed on this. A separate electrode was used in each test, and the 50 odd electrodes prepared matched each other within a millivolt in 31% potassium hydroxide. The reference value referred to hydrogen was 0.800 $\pm$0.001 volts in the 31% hydroxide at room temperature. Repeat measurements using the hydrogen electrode gave the same results within one millivolt. The hydrogen electrode is relatively unstable in strong caustic solutions.

The 31% potassium hydroxide solution was made by diluting reagent grade 45% solution; the sodium hydroxide solutions used were made up from reagent grade pellets. The carbonate impurity level in the dilute potassium hydroxide was 5-8% at start of cycling tests, and increased to ca. 10% at the end of the tests.

3.2 Electrode Preparation

Usually two electrodes were impregnated at the same time. The starting sintered plaques were marked for identification and weighed to 0.01 gram. They were then placed in a holder and inserted in a small resin jar that could be sealed, evacuated, and heated as desired. The assembled apparatus is shown in Figure 1. The heated separatory funnel at the top was used to bring the impregnation solution to temperature and was fitted with a stirrer (not shown) to assure complete mixing of the solutions just prior to adding them to the electrode holder. The holder was a Lucite box and is just barely visible above the top of the resin jar heating mantle inside the jar. A Tygon tube was used to direct the flow into the box. A stainless steel dial thermometer was used to measure the temperature.

The electrodes were heated to 65° - 70° under vacuum, and the pre-heated, well-stirred, nickel-nitrate impregnating solution was pulled into the electrode holder. The electrodes were allowed to soak under vacuum for 5 minutes, then the solution was removed and the electrodes were dried under vacuum for 20-30 minutes at 60-70°C. The electrodes were then immersed in warm 25% sodium hydroxide to convert the nitrates to hydroxides, and washed with distilled water. The electrodes were electrochemically cleaned to remove the final traces of nitrates by electrolysis at 1 ampere for 4 hours in 26% sodium hydroxide. The solution was then replaced, and the electrolysis repeated for one hour in fresh sodium hydroxide solution. The electrodes were then washed thoroughly with distilled water and dried in air at room temperature. The electrodes were then reweighed and were stored in closed containers until placed in a cell. This procedure closely follows plant practice except that only a single impregnation is used instead of the multiple ones normally performed. The single impregnation gives useful test results with minimum expenditure of time.

After assembly into a cell, the electrode was formed by charging at 100 ma for 16 hours and discharging at 100 ma for 8 hours.

3.3 Test Equipment

The test cell is shown in Figure 2. The cell housing is made of Lucite. In use, the test electrode is placed between two standard negative electrodes, with a reference electrode at one edge. The cell is filled with 31% potassium hydroxide, and sealed by waxing the Lucite cover on and plugging the holes with wax. Figure 3 shows the component parts of the cell. The reference electrode shown at the bottom of the figure fits into the center hole of the cell cover into a well in the holding block of the cell body. The electrodes are kept separated by using slotted holders.

The cells were charged and discharged at constant current, using standard current sources (Harrison 865B). The reference-test electrode potential was recorded using a Hewlett-Packard model 412 voltmeter as buffer amplifier and a Leeds and Northrup model H recorder. Cycling was controlled with a cam cycling timer and appropriate relays. Three cells could be tested at one time.

3.4 Test Procedure

One electrode from each pair was tested using a 100 ma discharge. The charge and discharge times were adjusted to give complete charge and discharge of the electrode. The 100 ma current corresponds to about a C/3 rate. Nine to ten test cycles per electrode were run. Figures 4 through 42 give the normalized curves for the tests; the curves for the nickel-hydroxide electrode without additive are shown for comparison. The normalization was on capacity; this allows direct comparison between the various electrodes and the charge-discharge parts of the cycle. The data used are for a typical curve for the electrode; the results were generally reproducible to ± 10 millivolts. Figures 43 through 53 give the curves for electrodes with selected additives at 50 ma charge and discharge. In these tests, the second electrode of the pair made was used.

These curves are presented so that the basic data generated in the project are available to other workers.

4.0 RESULTS

The voltages at midpoint of the charge or discharge curves were compared for each test. The 100 ma results are given in Table V, the 50 ma results are given in Table VI. In the tables, the per cent utilization was

TABLE V

SUMMARY OF 100 MA TESTS

Code	Name	Utilization %	Midpoint Voltage vs Hg, HgO Charge	Discharge	Diff.
A	None (1)	0.81	0.470	0.370	0.100
B	10 Co	0.76	0.460	0.350	0.110
	20 Co	0.76	0.440	0.340	0.100
C	10 Sc	0.53	0.490	0.380	0.110
	15 Sc	0.45	0.490	0.410	0.080
	20 Sc	0.42	0.490	0.440	0.050
D	10 Mg	0.79	0.490	0.400	0.090
	20 Mg	0.58	0.490	0.400	0.090
E	10 Mn	0.68	0.445	0.320	0.125
F	10 Ce	0.84	0.470	0.375	0.095
G	10 Fe	0.40	0.480	0.370	0.110
H	10 Cr	0.78	0.470	0.380	0.090
I	10 Al	0.70	0.470	0.390	0.080
	20 Al	0.96	0.460	0.370	0.090
J	10 Di	2.10	0.490	0.380	0.110
K	10 In	0.57	0.470	0.360	0.110
L	10 Mo	0.66	0.480	0.380	0.100
	20 Mo	0.74	0.470	0.380	0.100
M	10 VO	1.25	0.460	0.360	0.100
N	10 Y	0.74	0.460	0.360	0.100
	20 Y	0.70	0.480	0.370	0.110
O	10 Co Al	0.89	0.460	0.370	0.090
	20 Co Al	0.95	0.440	0.350	0.090
P	10 Ag Mo	0.51	0.420	0.350	0.070
Q	10 Cd Zr	0.88	0.470	0.360	0.110
R	10 Mg Al	0.67	0.470	0.375	0.095
	20 Mg Al	0.69	0.490	0.390	0.100
S	1 Os	0.92	0.480	0.360	0.120
T	1 Rh	0.39	0.510	0.420	0.090
U	1 Pd	0.89	0.460	0.360	0.100
V	1 Pt	1.10	0.470	0.370	0.100
W	1 Ru (2)	-	-	-	-
X	10 Co Mo X (3)	0.84	0.480	0.380	0.100
Y	10 Cu W X (3)	0.74	0.460	0.360	0.100
Z	10 Zn Ti X (3)	0.72	0.500	0.400	0.100
AA	10 Co Al X (3)	0.92	0.470	0.360	0.110
AB	10 Mg Al X (3)	0.91	0.425	0.380	0.095
AC	10 Li Al X (3)	0.91	0.490	0.380	0.110

Table V con't

Code	Name	Utilization %	Midpoint Voltage vs Hg, HgO Charge	Discharge	Diff.
AD	10 Cd Zr X (3)	1.20	0.480	0.380	0.100
AE	10 Co Cr X (3)	0.85	0.480	0.380	0.100
AF	10 ScR (4)	0.50	0.470	0.380	0.090
AG	15 ScR (4)	0.51	0.470	0.390	0.080
AH	20 ScR (4)	0.52	0.480	0.430	0.050
AI	10 G_a	1.04	0.460	0.360	0.100
AJ	1 IR	1.14	0.460	0.350	0.110

(1) Standard electrode for comparison

(2) Not run because of severe degradation of electrode plaque

(3) Preformed spinels added as fine powder to nickel nitrate impregnation solution

(4) Rerun of this additive

TABLE VI

SUMMARY OF 50 MA TESTS

Code	Name	Utilization %	Midpoint Voltage (1)					
			Charging		Discharge		Diff.	
			Pos	Cell	Pos	Cell	Pos	Cell
A	None	0.84	0.480	1.32	0.380	1.19	0.100	0.13
D	10 Mg	0.92	0.510	1.40	0.410	1.26	0.100	0.14
I	20 Al	1.20	0.460	1.32	0.370	1.19	0.090	0.13
J	10 Di	2.62	0.475	1.32	0.360	1.18	0.115	0.14
O	20 Co Al	1.02	0.450	1.36	0.365	1.24	0.085	0.12
P	10 Ag Mo	0.81	0.455	1.32	0.355	1.19	0.100	0.13
R	10 Mg Al	0.95	0.480	1.34	0.380	1.22	0.100	0.12
T	1 Rh	0.87	0.460	1.32	0.370	1.21	0.090	0.11
Z	10 Zn Ti X (2)	0.91	0.485	1.37	0.390	1.26	0.095	0.11
AF	10 ScR (3)	0.24	0.530	1.33	0.485	1.21	0.085	0.12
AG	15 ScR	0.52	0.490	1.38	0.410	1.26	0.080	0.12
AH	20 ScR	0.70	0.495	1.32	0.410	1.17	0.085	0.15

(1) Positive electrode values vs Hg, HgO references.

(2) Solid Spinel added as fine powders

(3) Rerun

calculated by assuming that the weight gain exhibited by the electrode was all due to formation of nickel hydroxide; the theoretical capacity for the electrode was calculated from this weight. The actual capacity was determined from the discharge curve. The true theoretical capacity is actually very difficult to determine without destruction of the electrode, since some of the nickel in the sinter is corroded during impregnation. A utilization of 75-85% is normal for fully impregnated electrodes.

The results show that only scandium gives an appreciable reduction in the voltage difference; however, scandium electrodes show poor utilization. The use of spinels is thus not beneficial to electrode performance with respect to decreasing the voltage difference.

The effect of the additives on the charge curve is of interest. Some of the additives, e.g. scandium, aluminum, magnesium, etc. give curves in which the voltage rises to a final value without a marked inflection; others, e.g., cobalt, cerium, didymium, etc. show a marked inflection in the curve.

The specific summary of the effect of each additive follows:

Cobalt - This is a standard additive in commercial cells. Its use is based on the improved capacity shown by the positive electrodes on cycling, and improved charge retention. No effect on reversibility is observed.

Scandium - Only a part of the results reported by Doran are confirmed. The marked reduction in capacity is noteworthy. In general, both the charge and discharge voltage curves are elevated; this effect is more pronounced for the 50 ma tests.

Magnesium - Only a modest improvement in voltage difference is shown; capacity is maintained. An increase in electrode discharge voltage is obtained.

Manganese - This is the only additive found which increased the voltage difference significantly, and lowered the cell voltage.

Cerium - No effect on voltage difference or capacity.

Iron - This additive markedly lowers the capacity; this result has been observed in previous work.

Chromium - This additive gave electrodes that required up to six charge-discharge cycles before reproducible behavior was obtained. Chromate was observed (by color) in the electrolyte during these first cycles that gave erratic results; no deposition of chromium (III) was observed on the negative electrode.

Aluminum - Some reduction in charging voltage noted, with a reduction in voltage difference. Capacity retained.

Didymium - The results using this additive are puzzling. Its effect on cell voltage and voltage difference is very small; however, the utilization is excessively large. This increase in capacity cannot be explained by presence of an oxidation-reduction couple in the additive, since only cerium and praesodymium are known to charge valence readily and these are present only in small amounts. A massive attack on the nickel sinter during impregnation could explain the results; approximately 50% of the sinter would have to be attacked to account for the capacity. Visual inspection of the test electrodes,however, did not show more than the normal amount of attack. Time did not permit further investigation.

Indium - No effect on voltage difference and capacity.

Molybdenum - No effect on voltage difference and small apparent loss of capacity.

Vanadyl - No effect on voltage difference; the large utilization is probably due to attack on the nickel sinter.

Yttrium - No effect on voltage difference or capacity.

Cobalt Aluminate - Some reduction in charge voltage, and increase in capacity.

Silver Molybdate - The electrode behavior corresponds to a composite silver oxide-nickel hydroxide electrode.

Magnesium Aluminate - No effect on voltage difference and some loss in capacity.

Platinum metals - No specific effect on voltage difference or capacity except for rhodium. In the 100 ma test, the rhodium electrode voltage was quite high; the second electrode used in the 50 ma tests failed to reproduce this effect. The marked decrease in capacity may be related to the voltage effect. Repeats of the impregnation also failed to confirm the first electrode results.

Spinels - No specific effect on voltage difference or capacity was observed. Zinc titanate gave an appreciable discharge voltage rise at 100 ma which is confirmed by the 50 ma test.

Gallium - No effect on voltage difference or capacity.

Ten experimental cells with nickel hydroxide-additives electrodes were prepared and shipped to the customer. Table VII shows the data on

TABLE VII

EXPERIMENTAL CELL DATA

Cell	Additive	Capacity	Voltage Difference at Midpoint	End of Discharge Voltage (1)
1	15 Sc	2.0	0.16	1.08
2	15 Sc	2.1	0.15	1.17
3	15 Sc	2.2	0.16	1.10
4	15 Sc	2.0	0.16	1.11
5	10 Di	4.1	0.18	1.16
6	10 Di	3.6	0.12	1.11
7	10 Mg	2.5	0.15	1.10
8	10 Mg	3.1	0.15	1.10
9	10 Mg	2.7	0.14	1.16
10	10 Mg	3.0	0.13	1.12

(1) Voltage at knee of discharge curve.

these cells. Figure 54 shows a picture of nine of these cells. These cells are standard BB403 (nominal 4AH capacity) size and configuration. The electrodes were given 6 impregnations, and standard negative electrodes were used. The additives used were selected on the basis of raising the cell voltage in the scandium and magnesium cases, and the peculiar capacity effect in the case of didymium. The effect in the latter is not observed for the multiple impregnated electrodes.

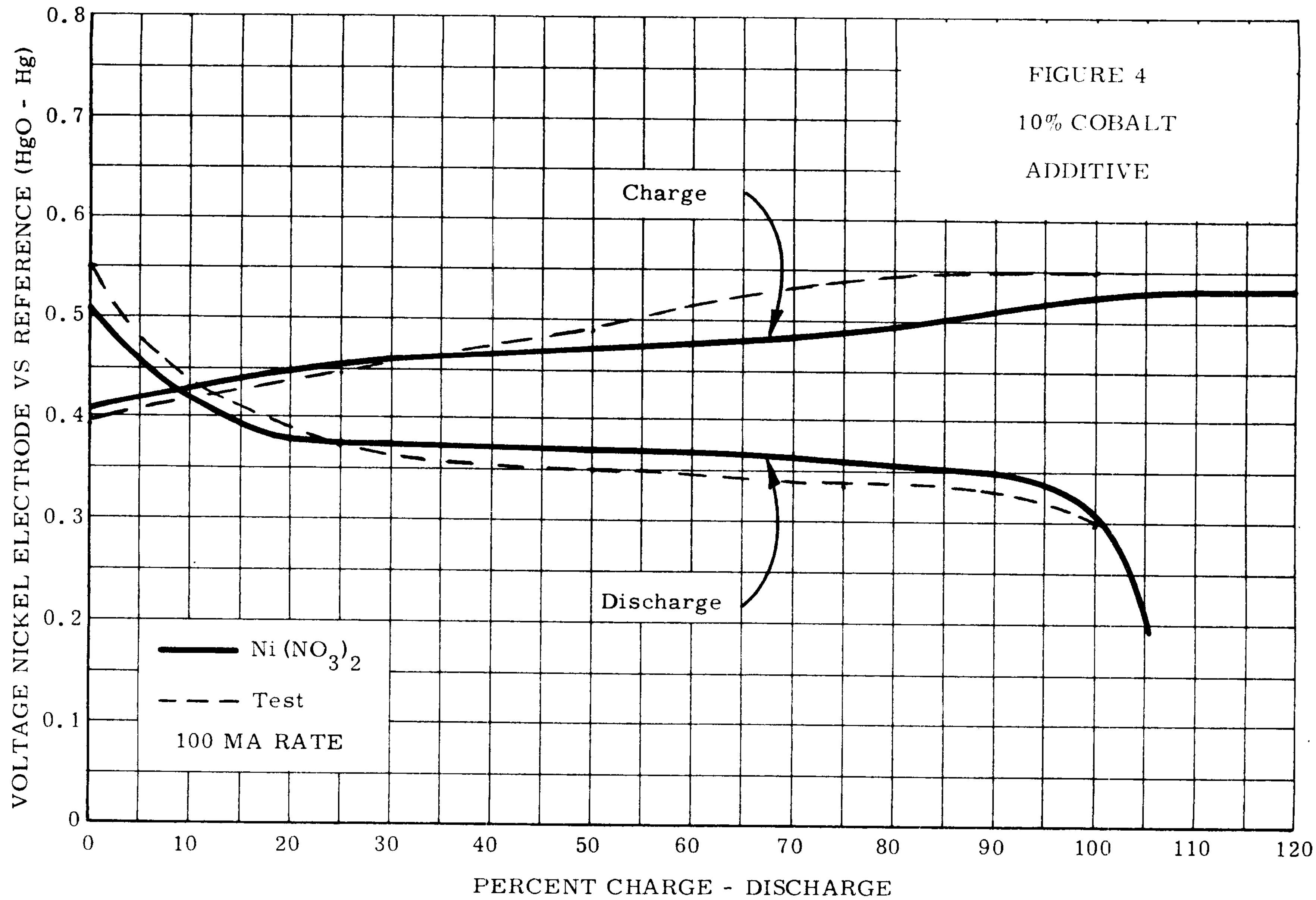

FIGURE 4
10% COBALT
ADDITIVE

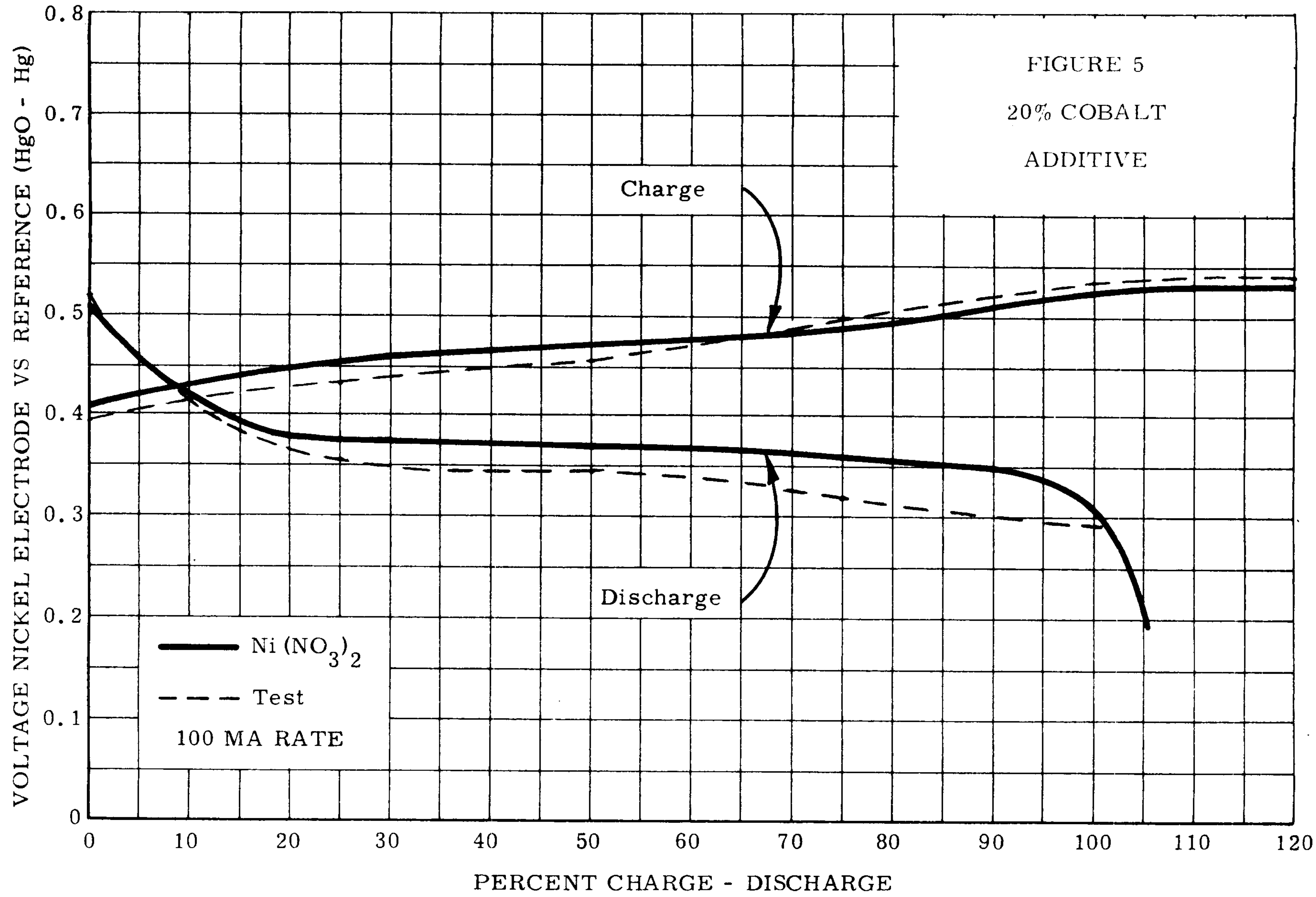
FIGURE 5
20% COBALT
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
PERCENT CHARGE - DISCHARGE

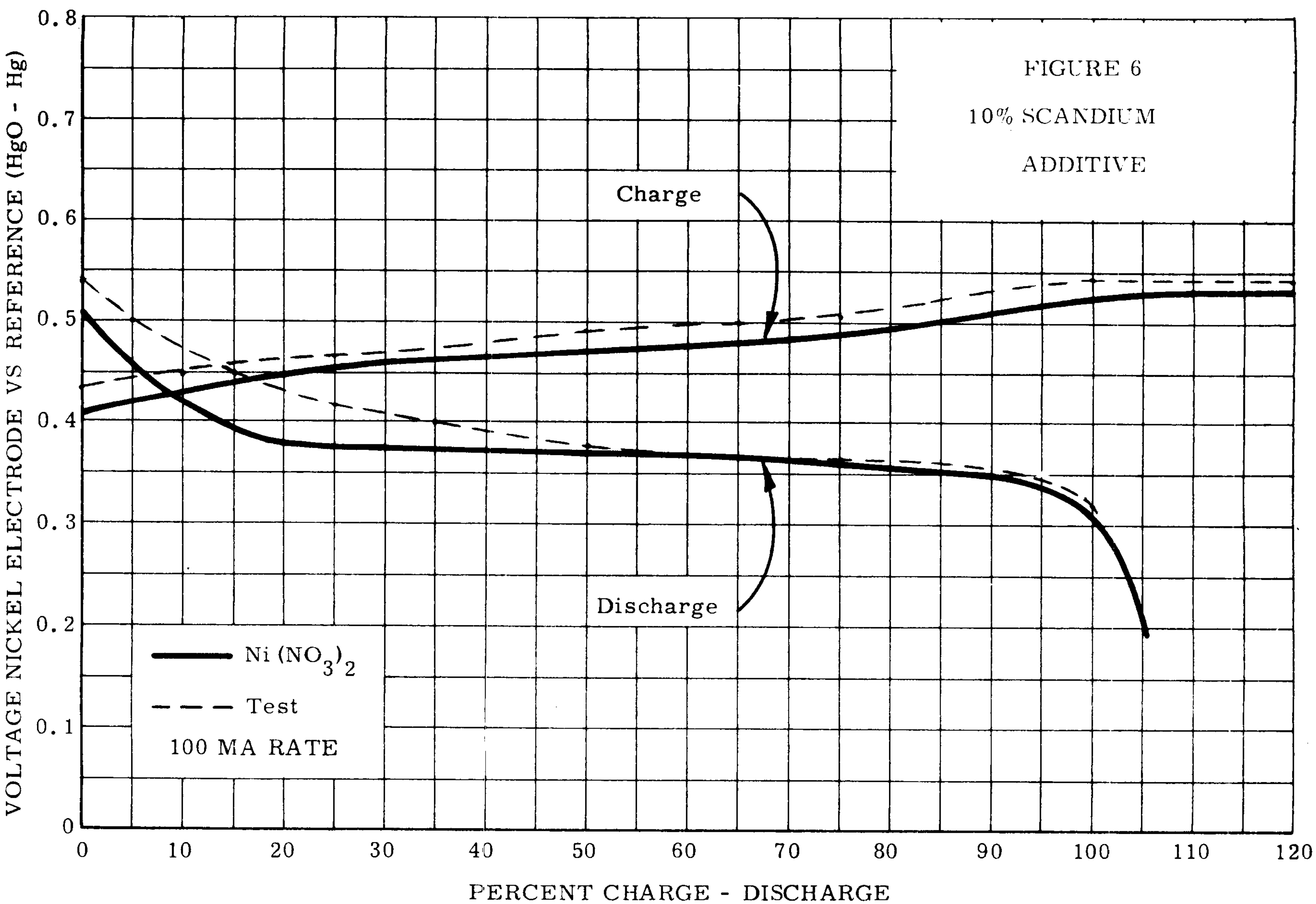
FIGURE 6
10% SCANDIUM
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
PERCENT CHARGE - DISCHARGE

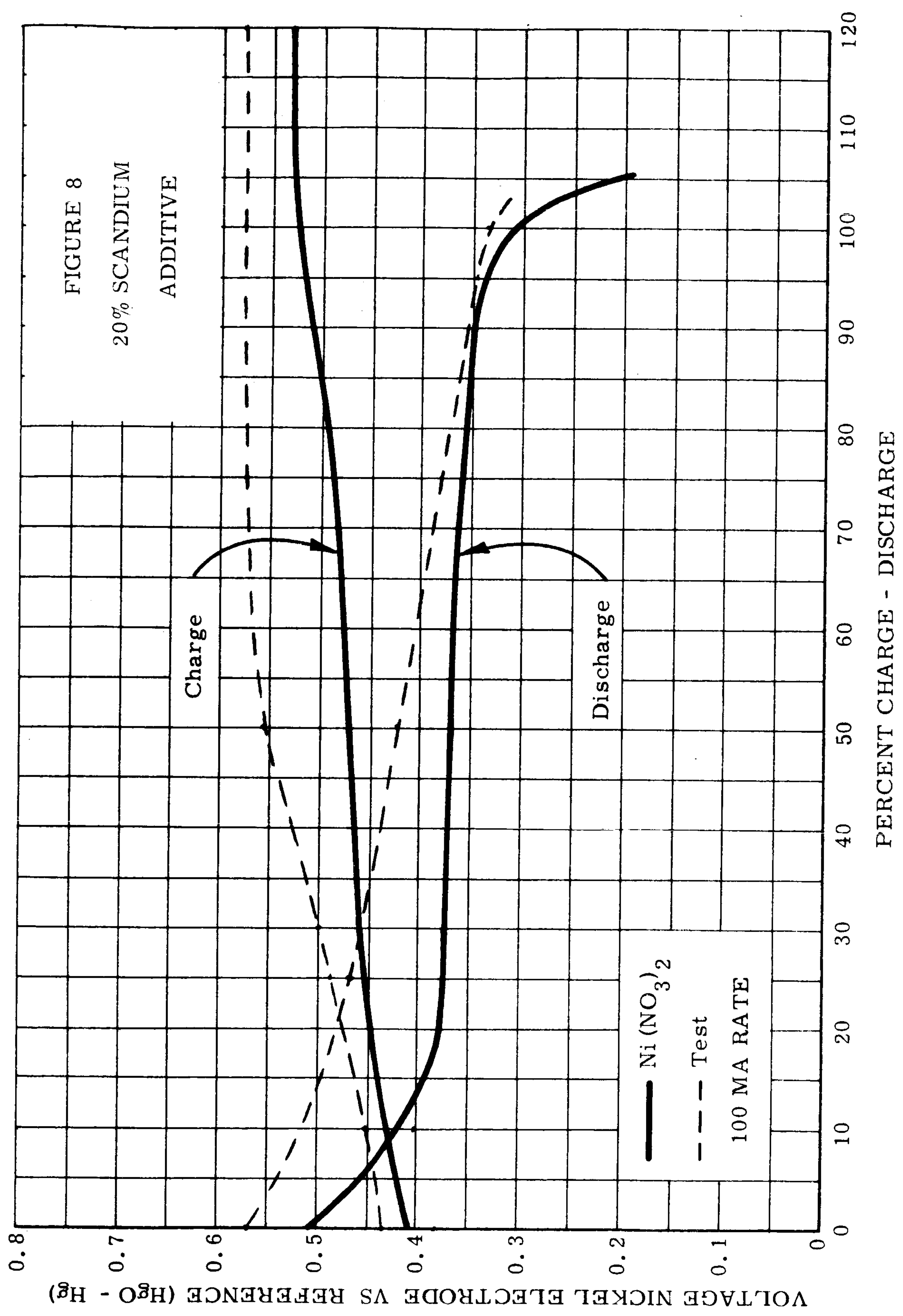
FIGURE 8
20% SCANDIUM
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
0
10
20
30
40
50
60
70
80
90
100
110
120
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)

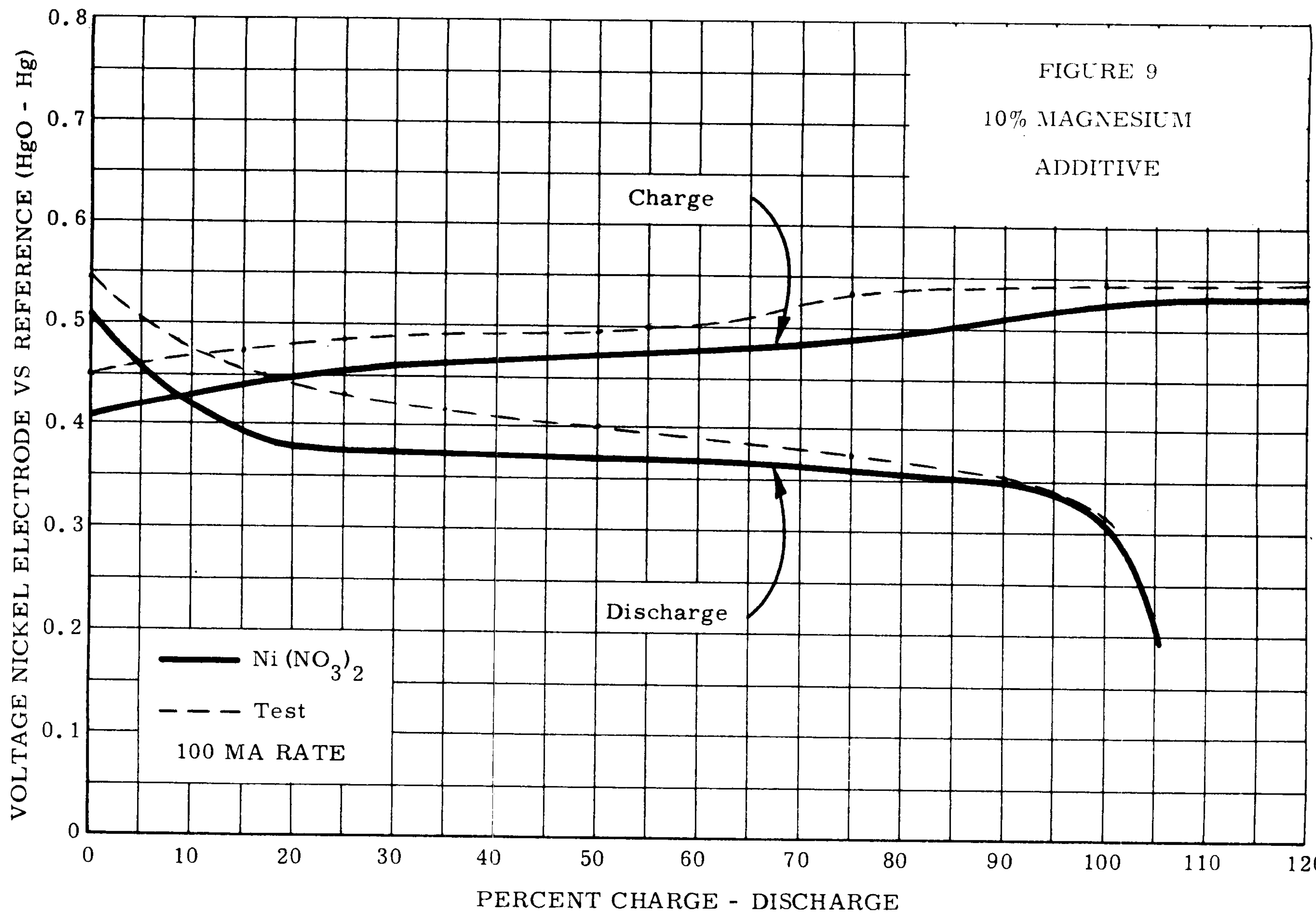

FIGURE 9
10% MAGNESIUM
ADDITIVE

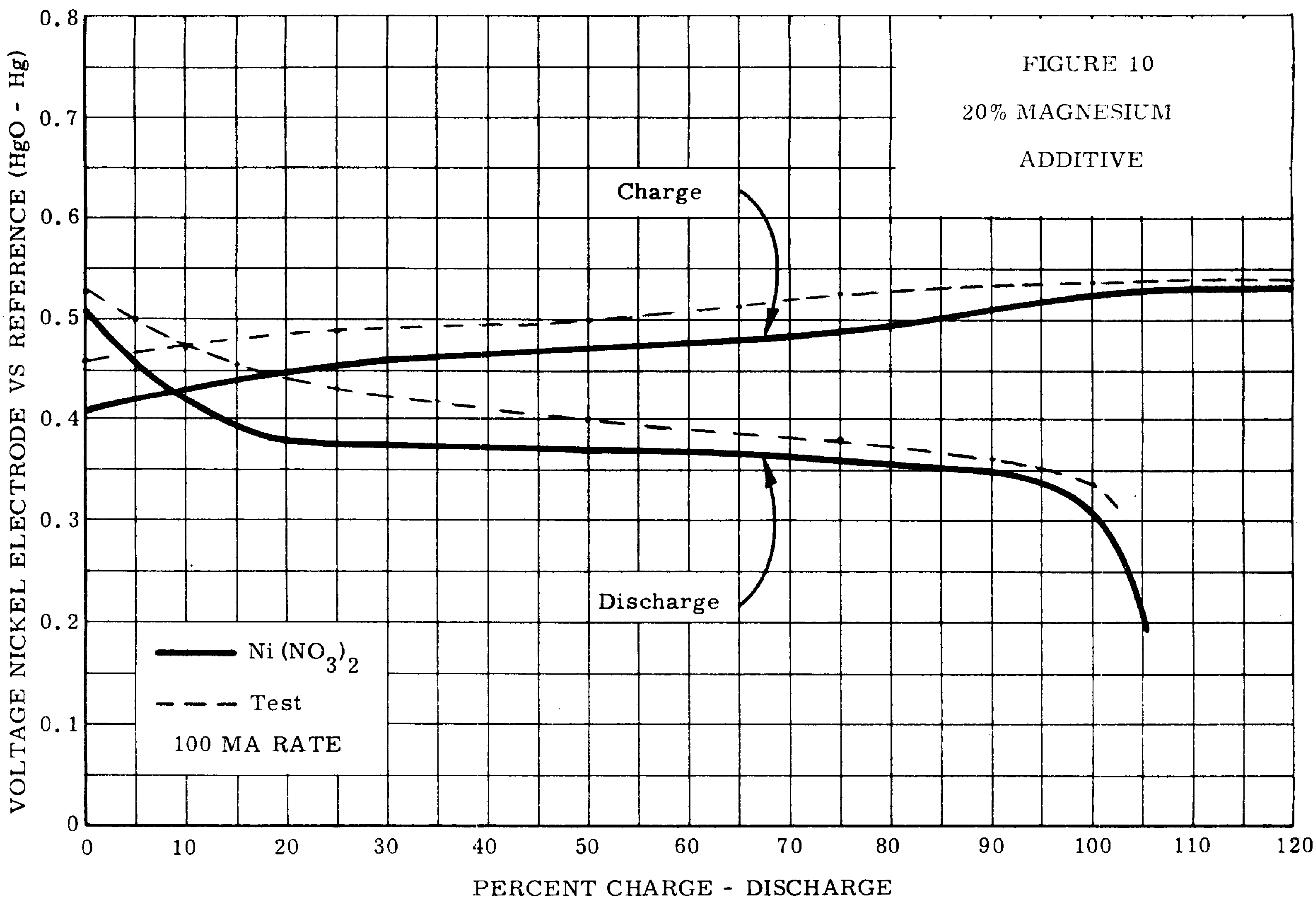
FIGURE 10
20% MAGNESIUM
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
100
110
120

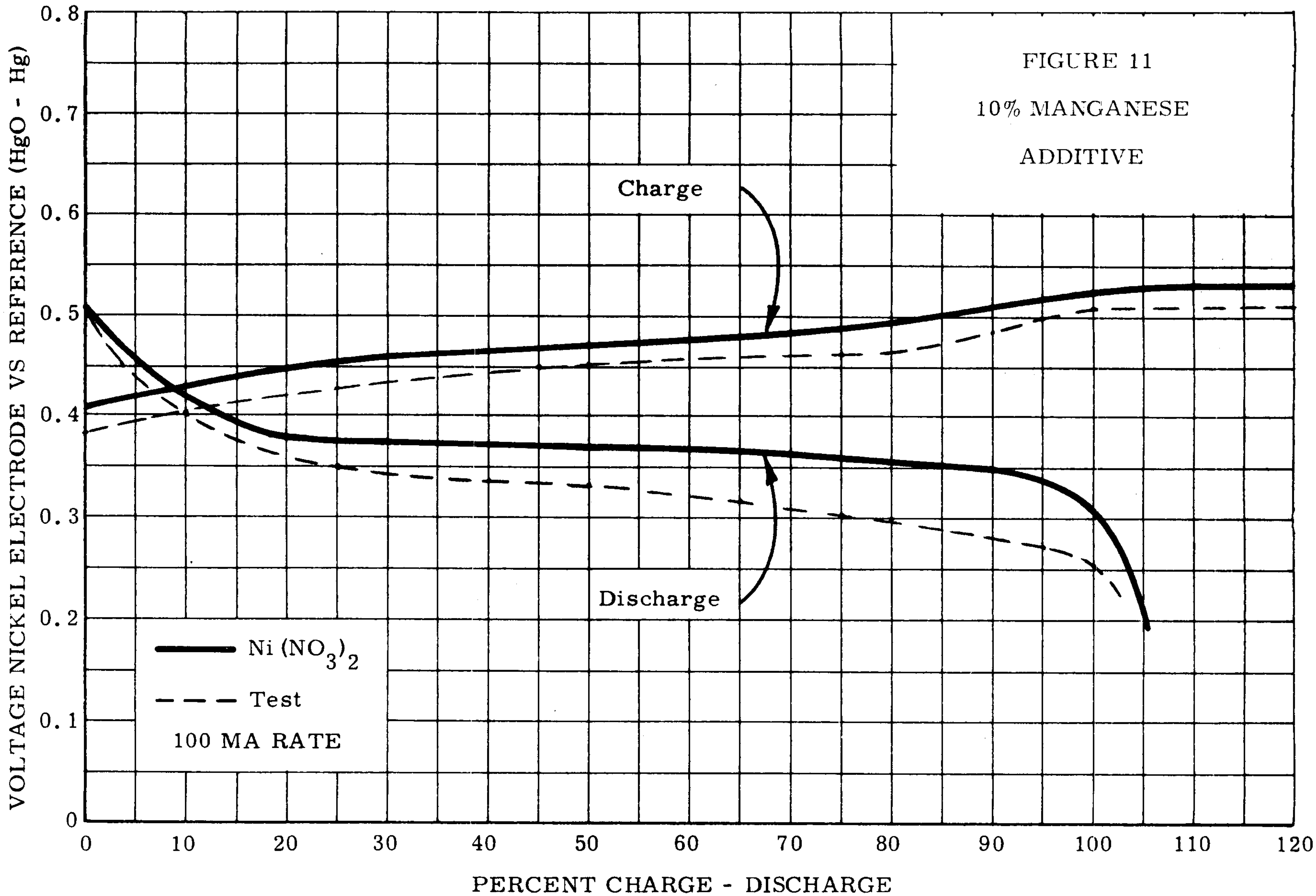
FIGURE 11
10% MANGANESE
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
PERCENT CHARGE - DISCHARGE

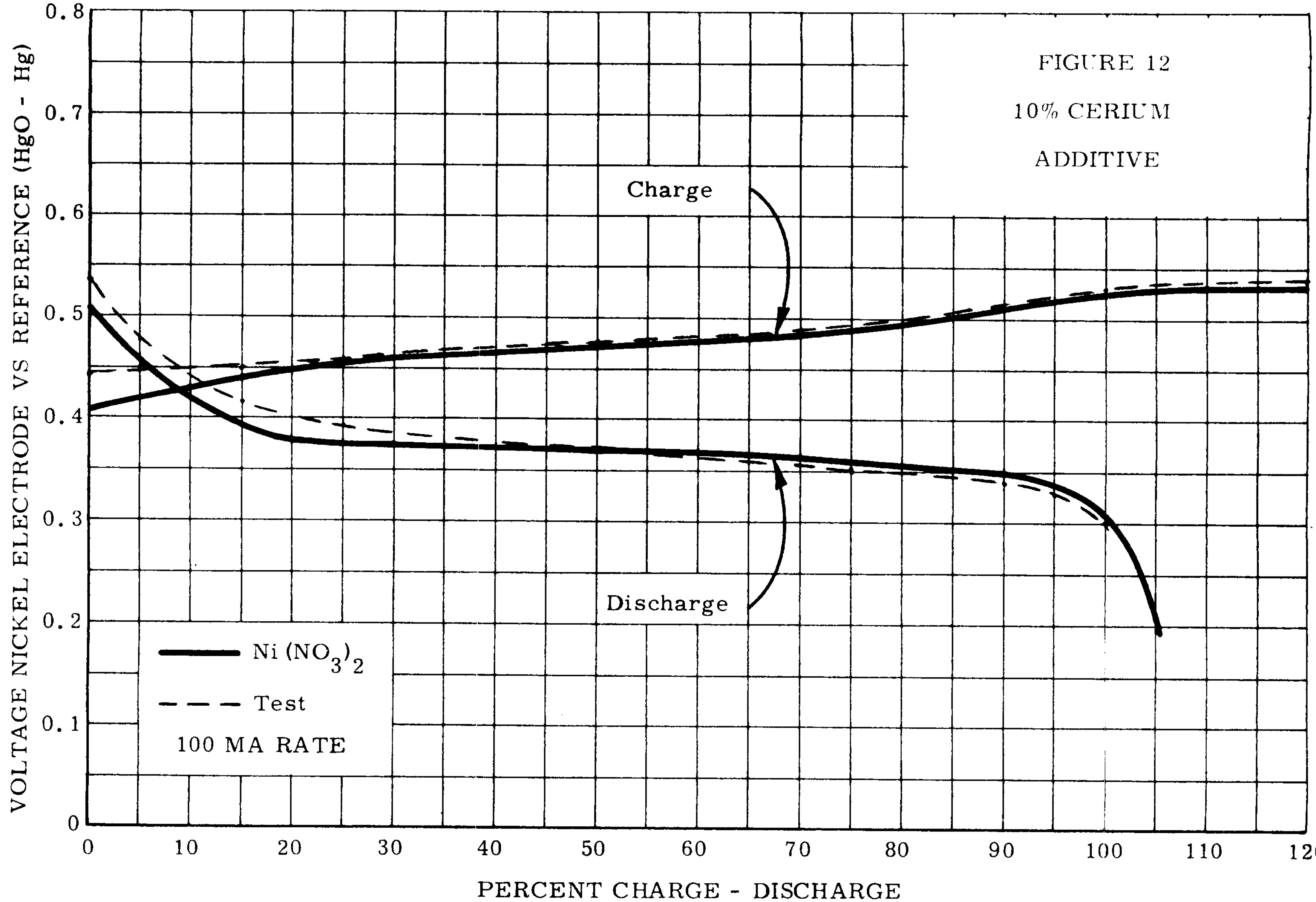
FIGURE 12
10% CERIUM
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
10
20
30
40
50
60
70
80
90
100
110
120

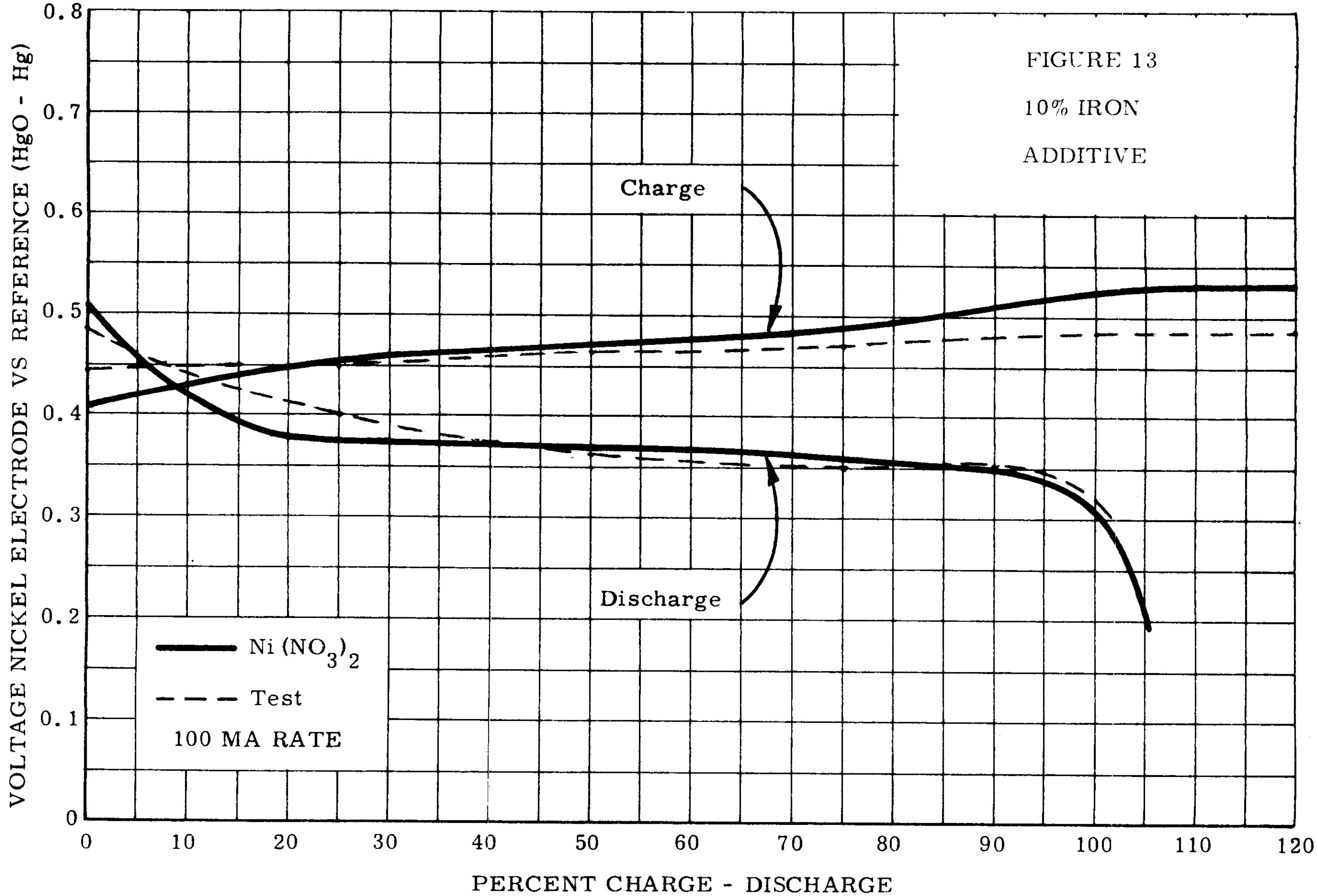
FIGURE 13
10% IRON
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE

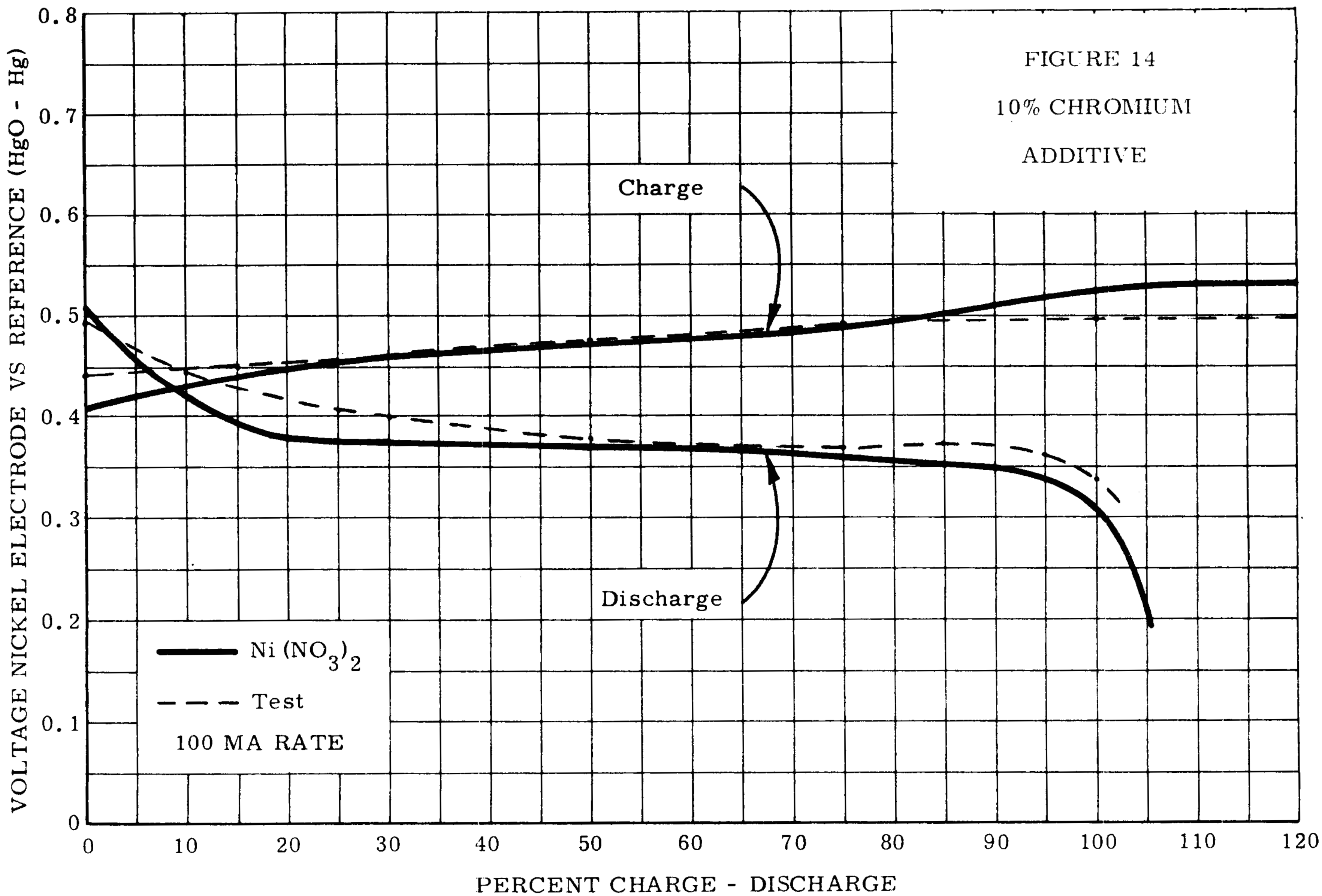
FIGURE 14
10% CHROMIUM
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120

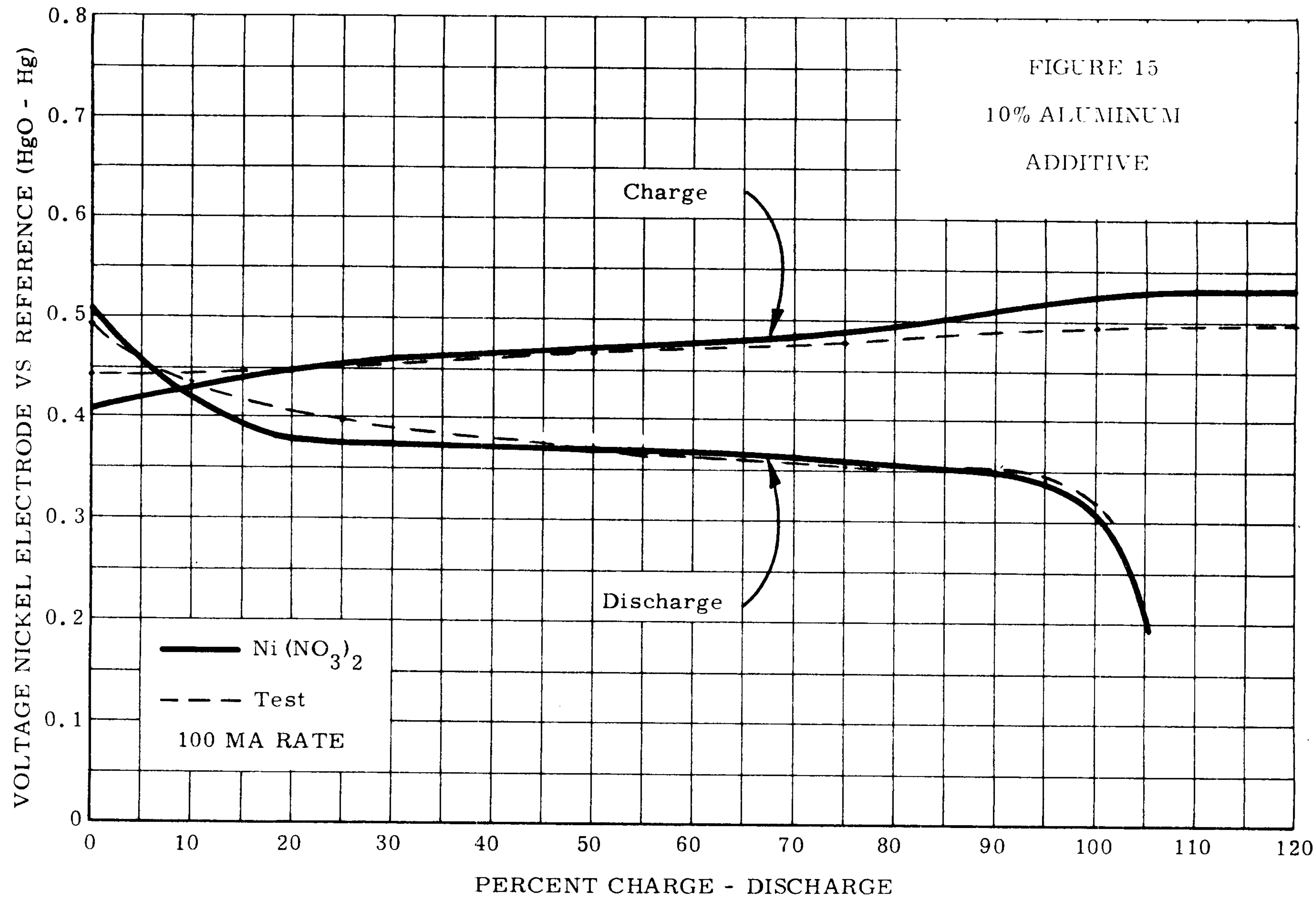
FIGURE 15
10% ALUMINUM
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
PERCENT CHARGE - DISCHARGE

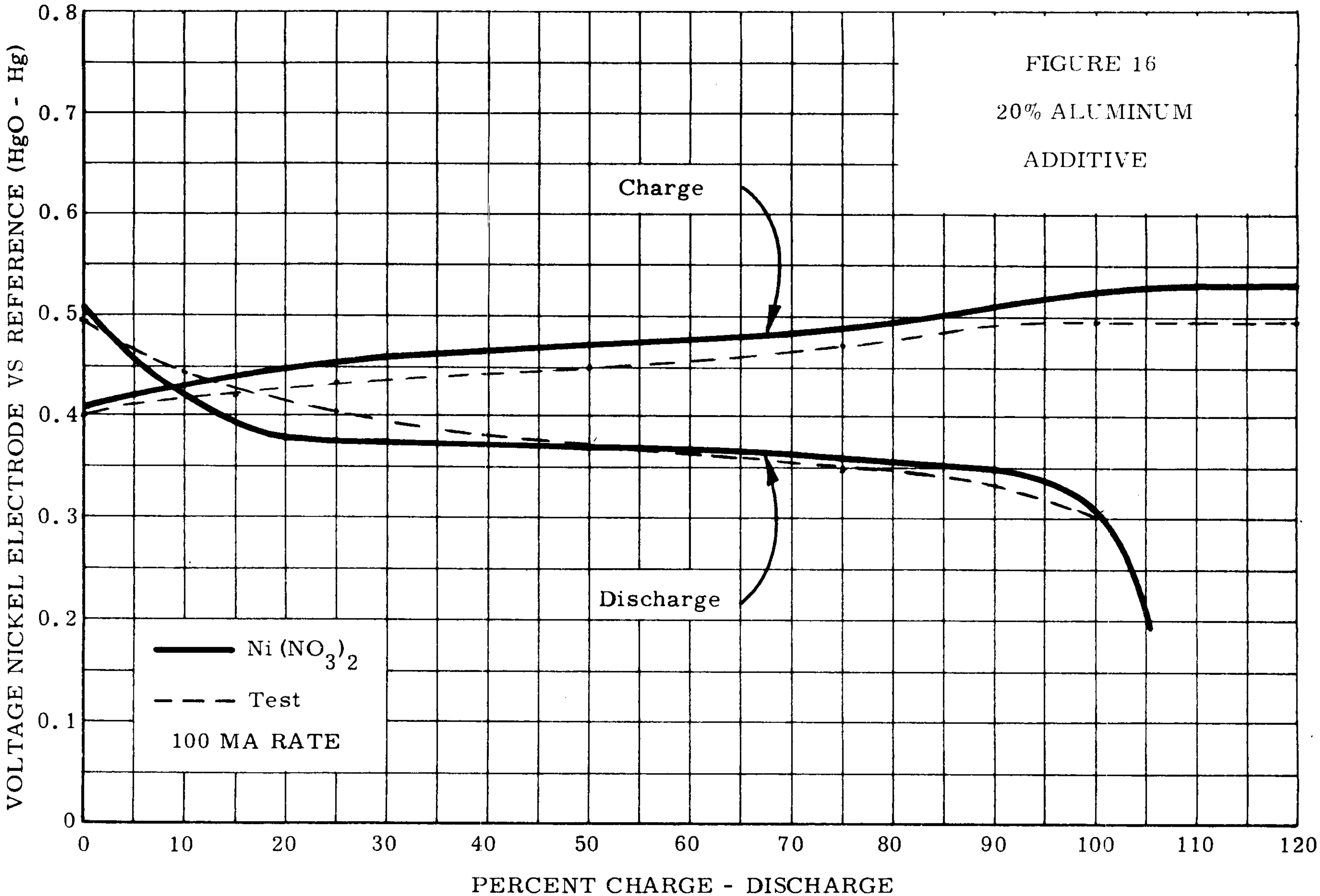

FIGURE 16
20% ALUMINUM
ADDITIVE

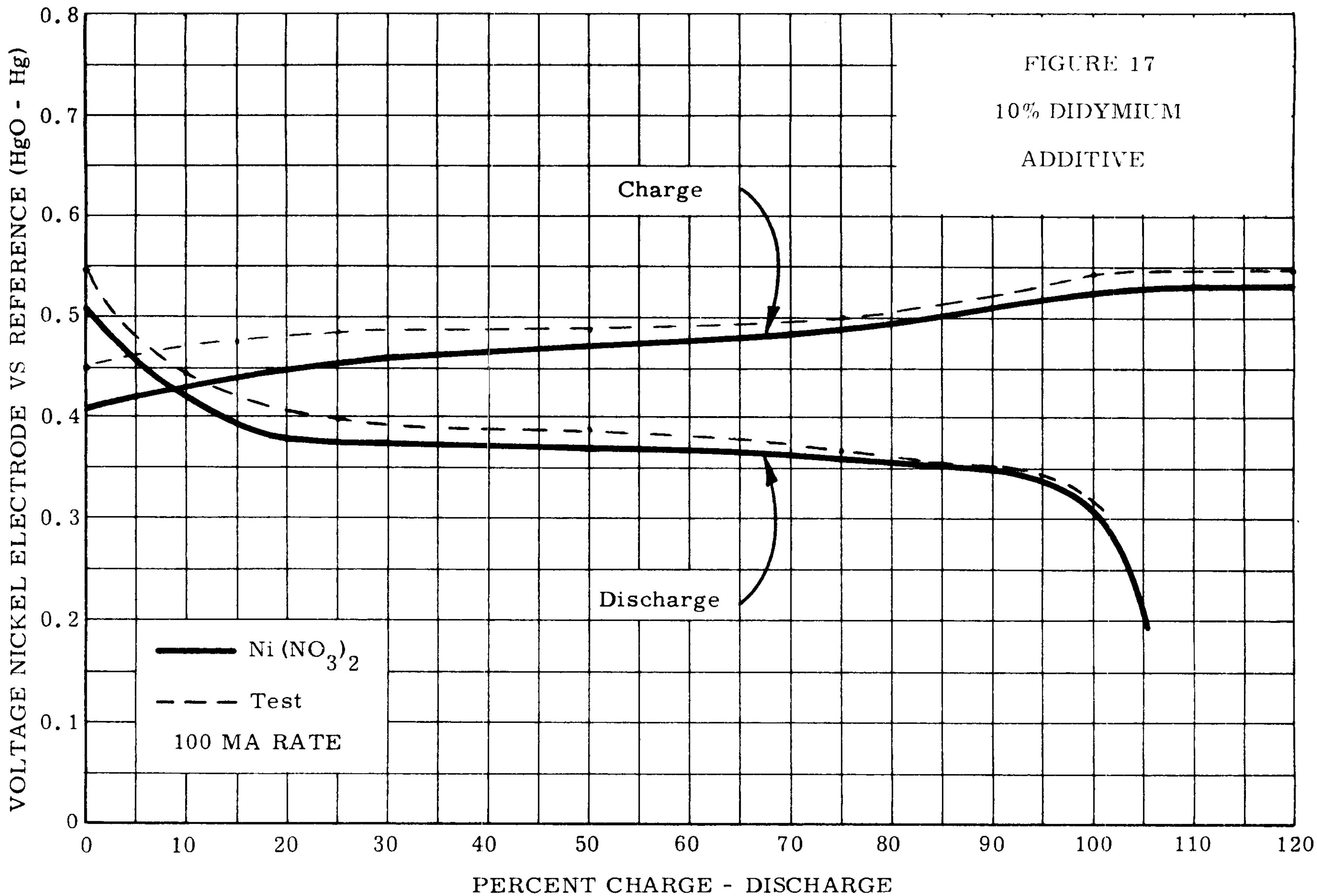
FIGURE 17
10% DIDYMIUM
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE

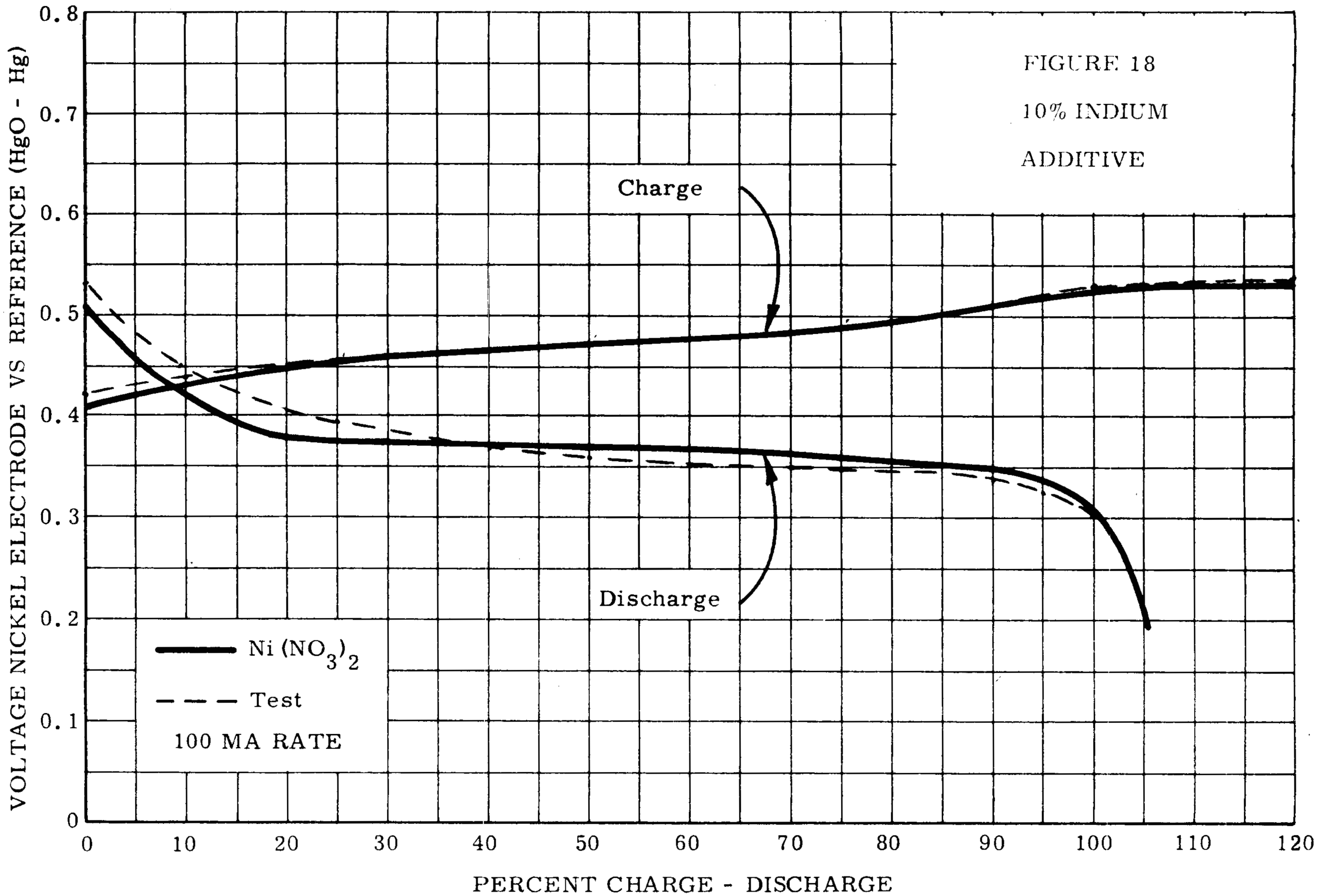

FIGURE 18
10% INDIUM
ADDITIVE

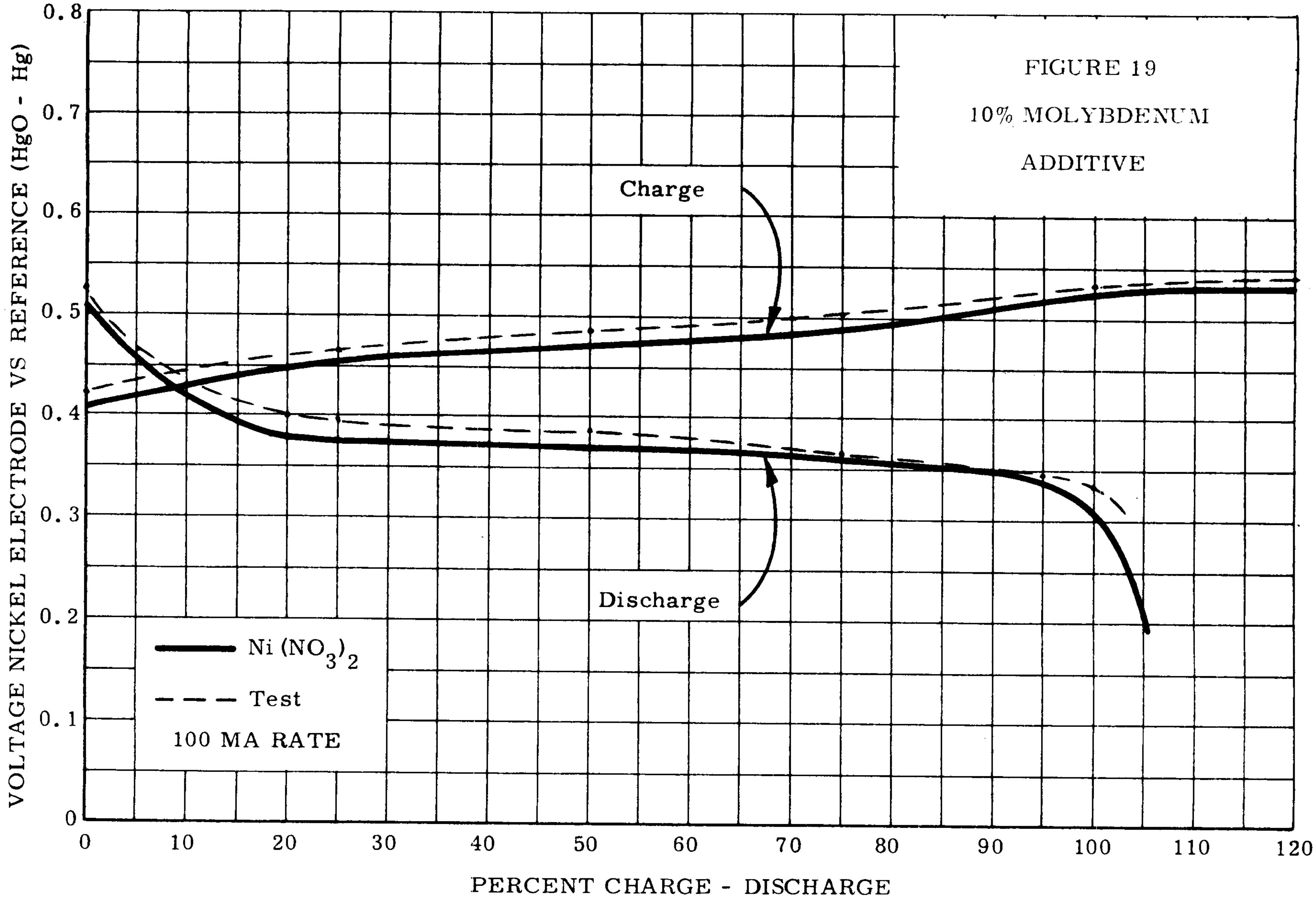
FIGURE 19
10% MOLYBDENUM
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
PERCENT CHARGE - DISCHARGE

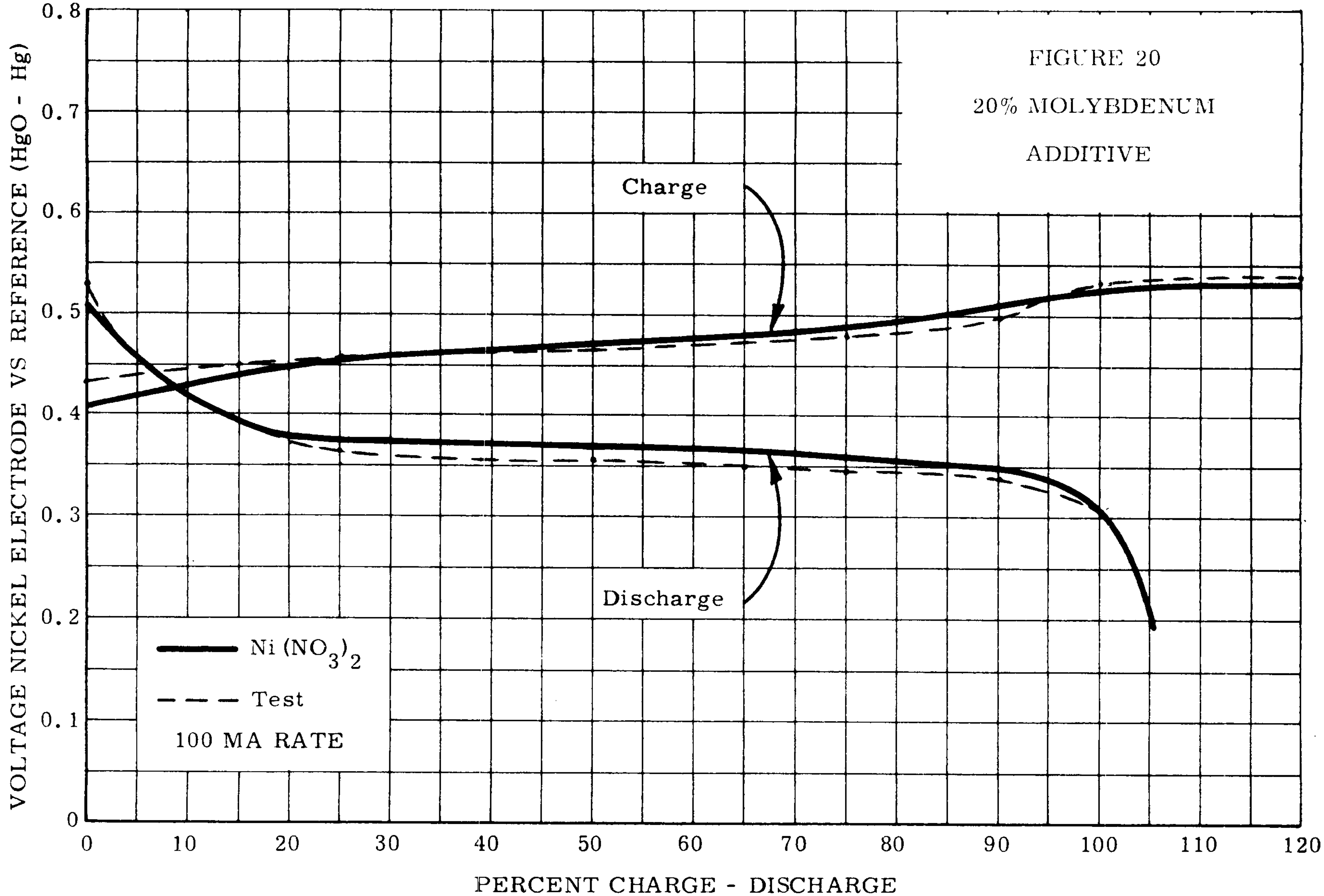
FIGURE 20
20% MOLYBDENUM
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
10
20
30
40
50
60
70
80
90
100
110
120

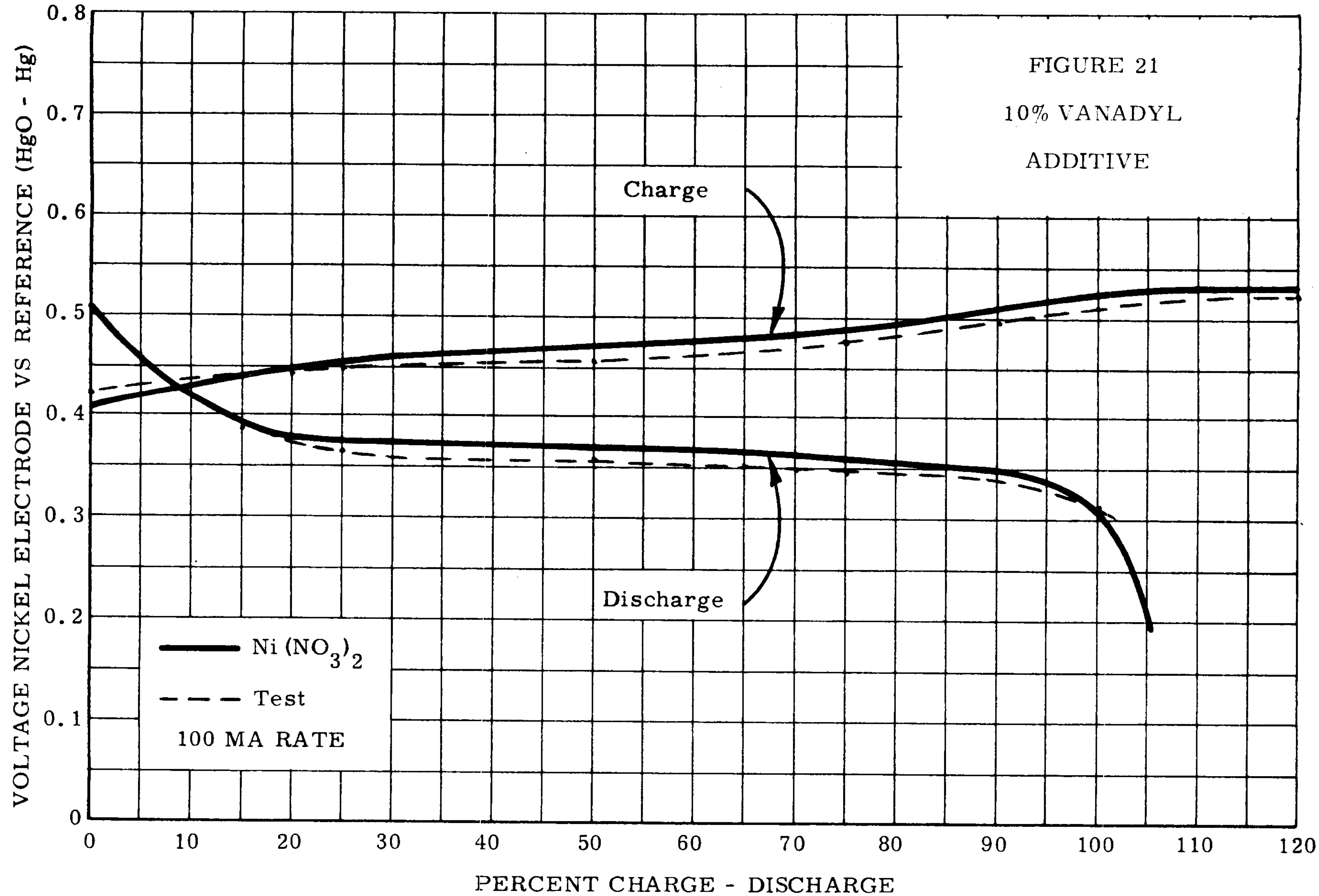
FIGURE 21
10% VANADYL
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
10
20
30
40
50
60
70
80
90
100
110
120

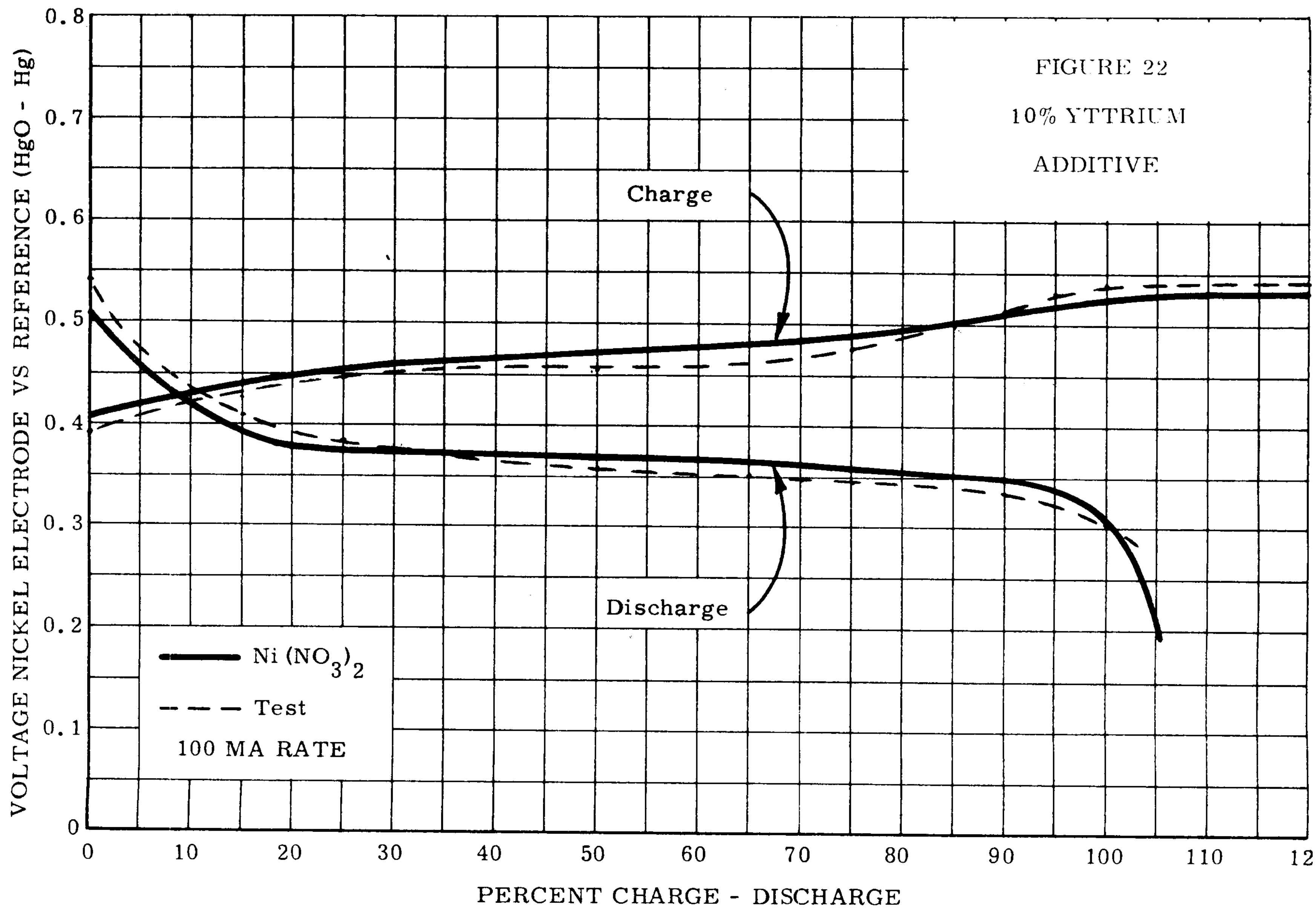
FIGURE 22
10% YTTRIUM
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE

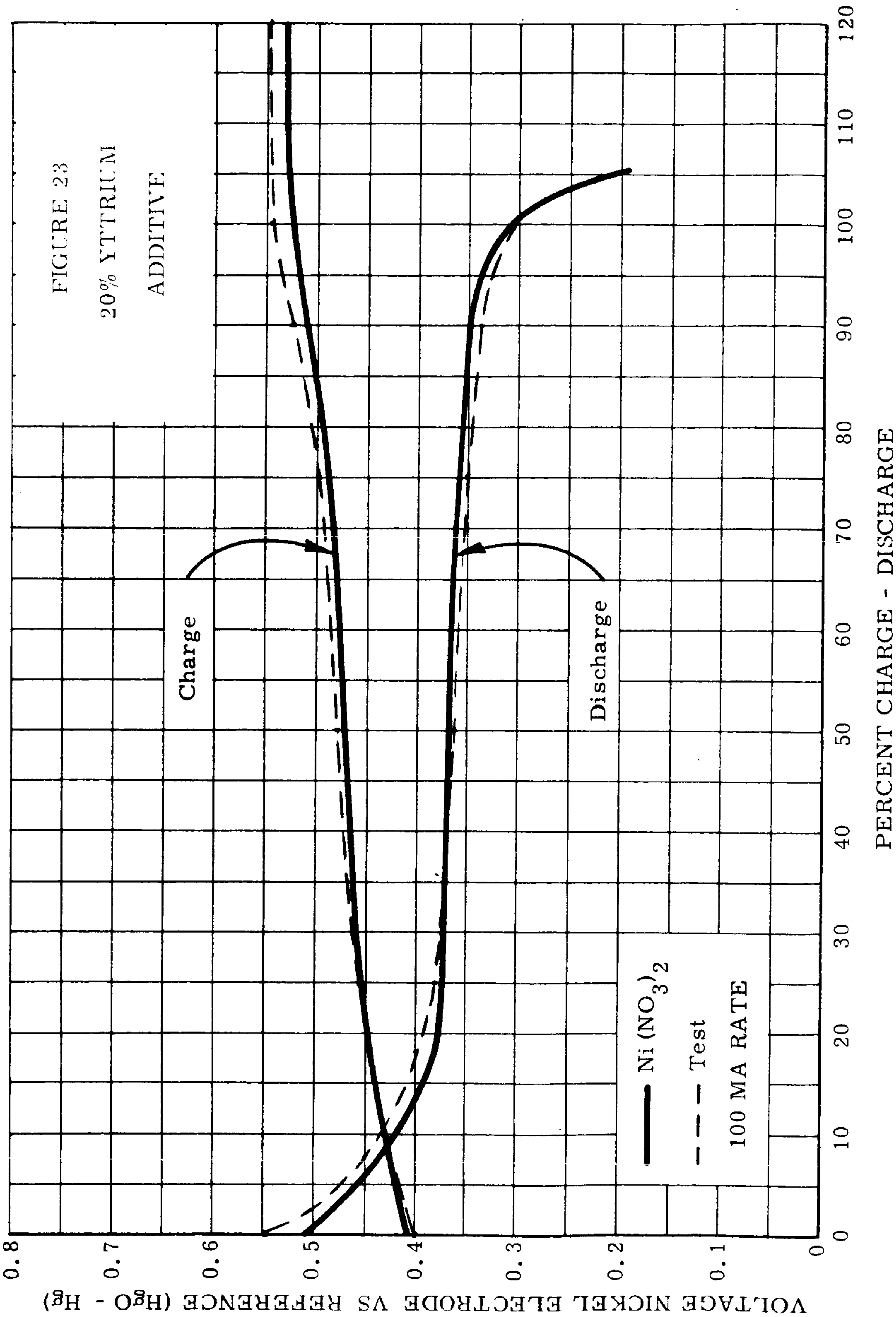

FIGURE 23
20% YTTRIUM
ADDITIVE

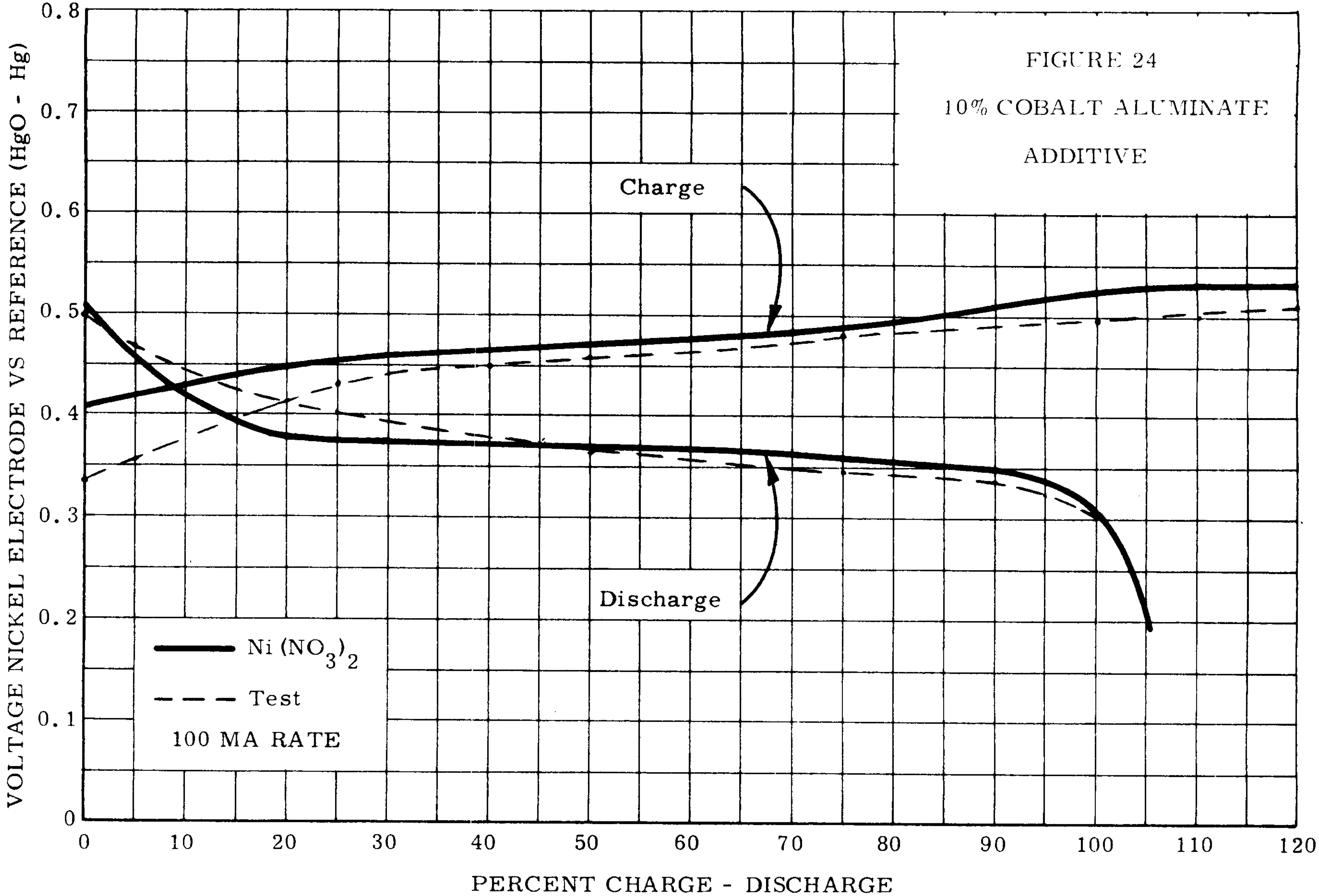

FIGURE 24
10% COBALT ALUMINATE ADDITIVE

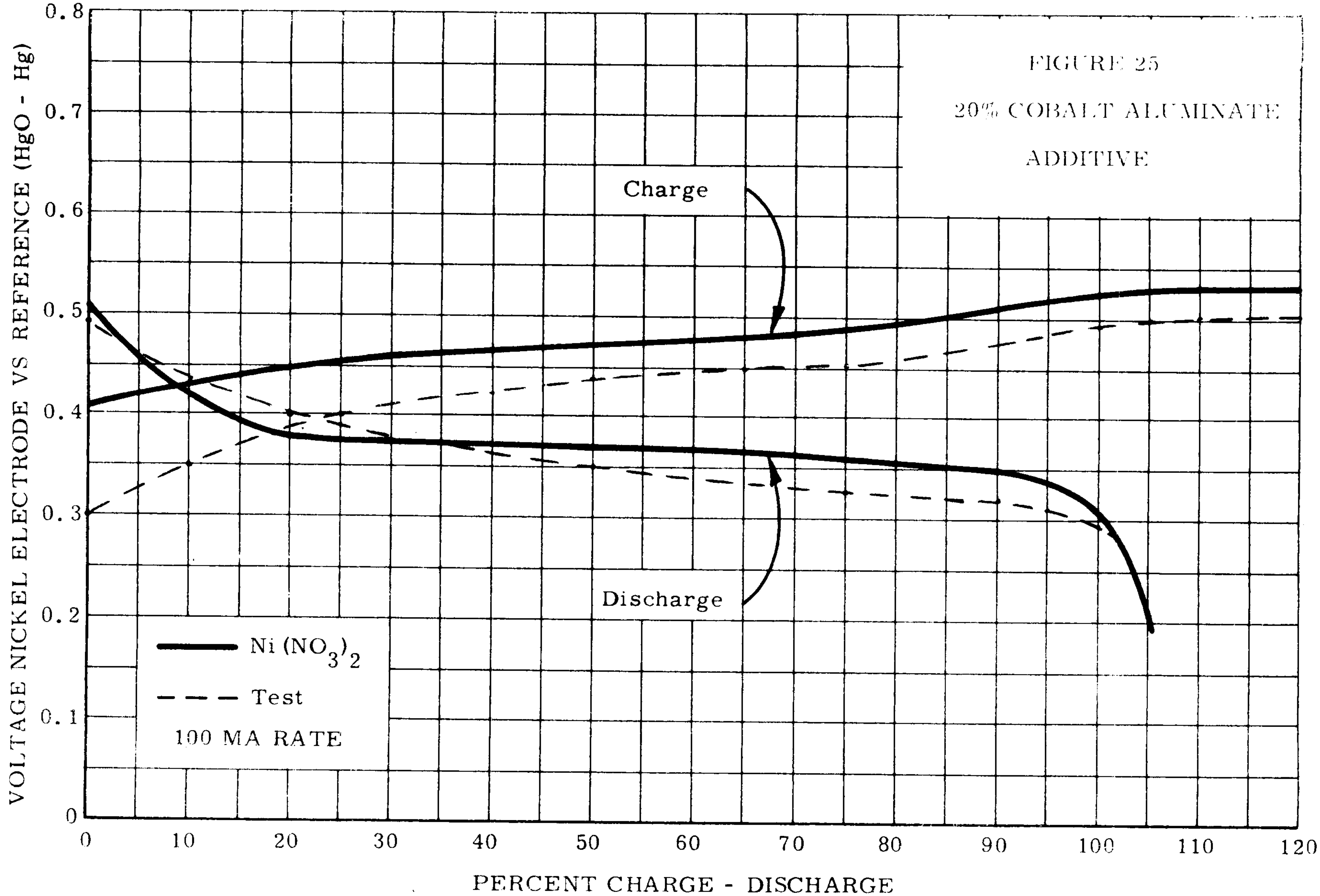

FIGURE 25
20% COBALT ALUMINATE ADDITIVE
Charge
Discharge
Ni (NO$_3$)$_2$
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
10
20
30
40
50
60
70
80
90
100
110
120

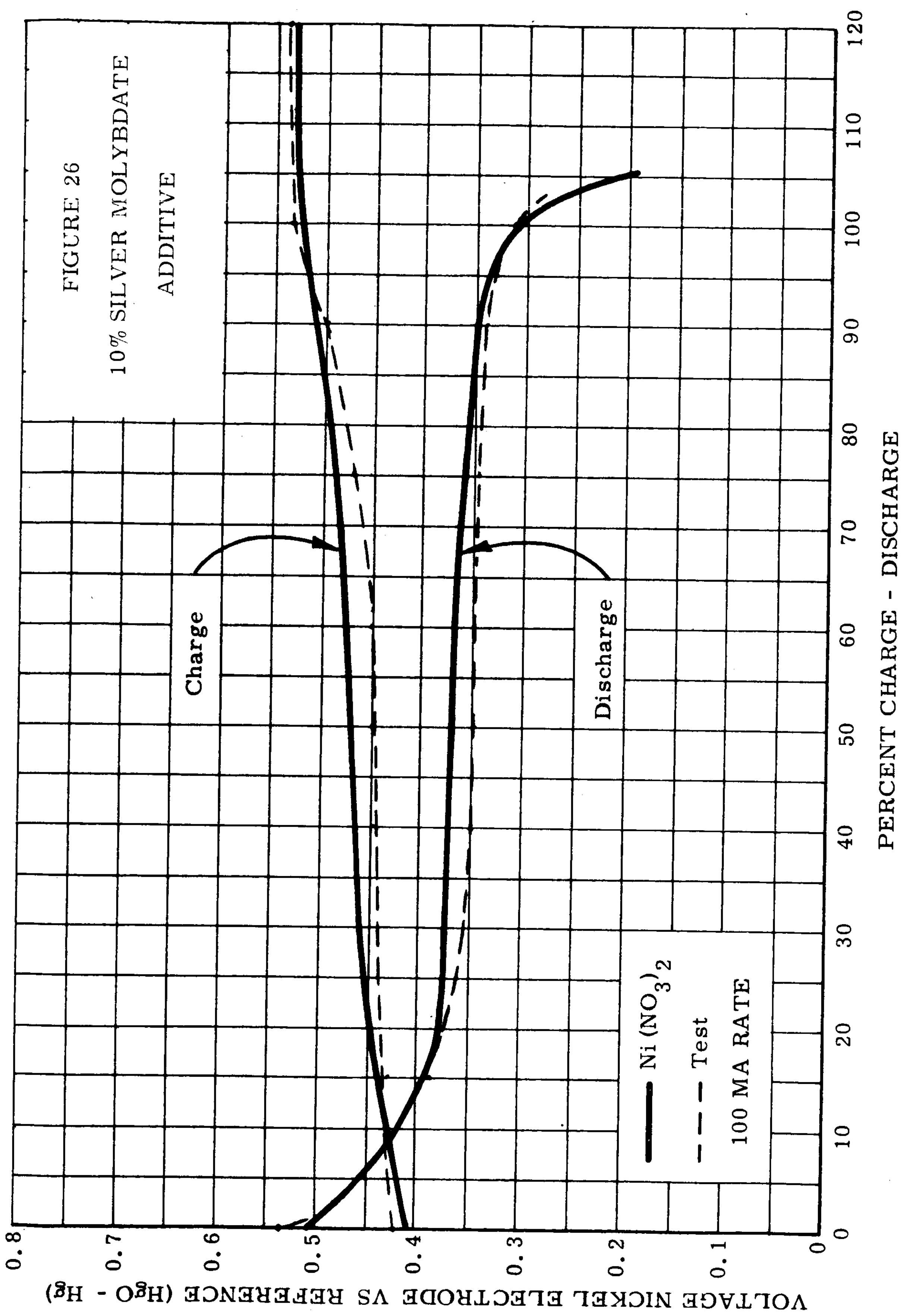

FIGURE 26
10% SILVER MOLYBDATE ADDITIVE

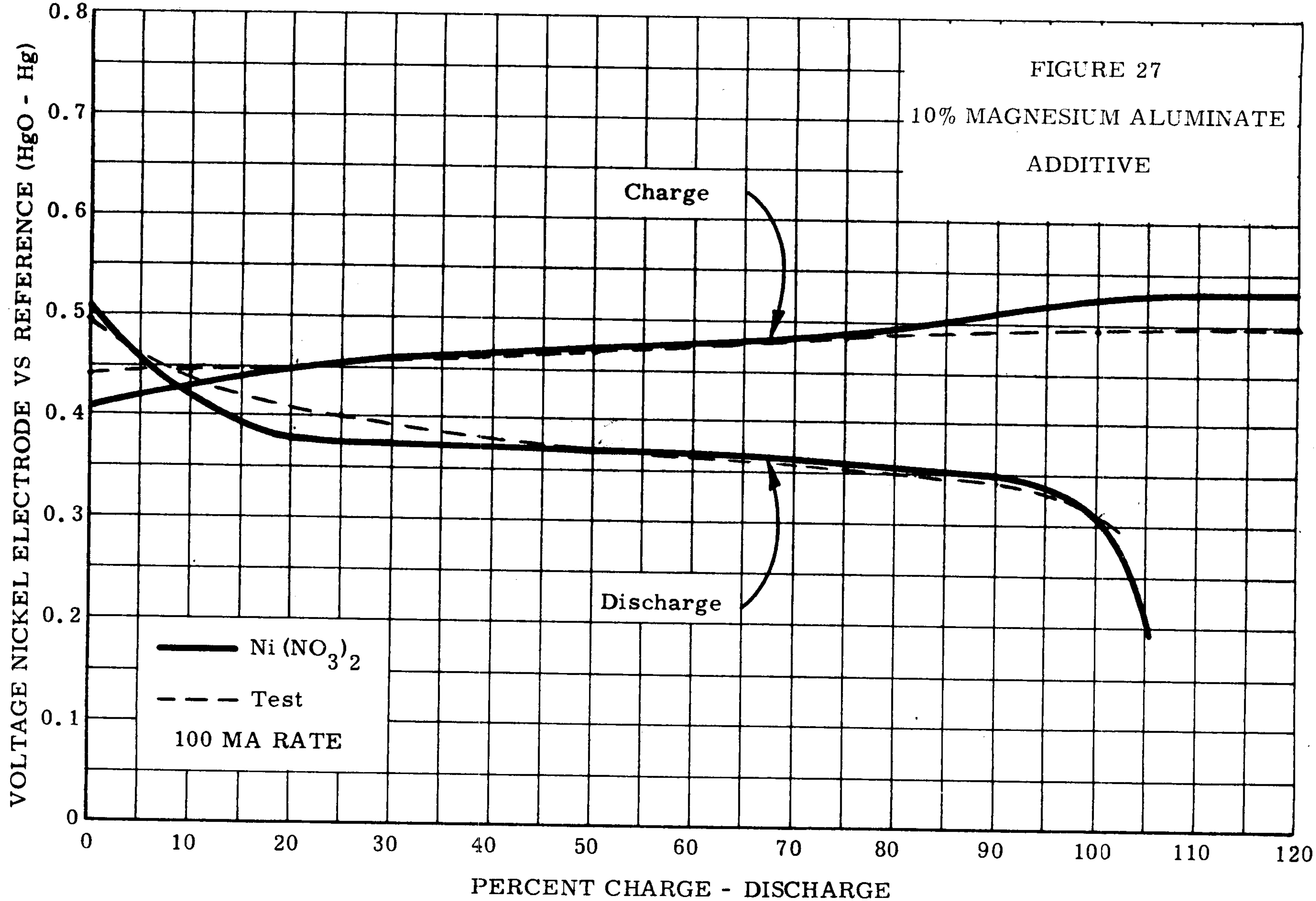
FIGURE 27
10% MAGNESIUM ALUMINATE
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
10
20
30
40
50
60
70
80
90
100
110
120

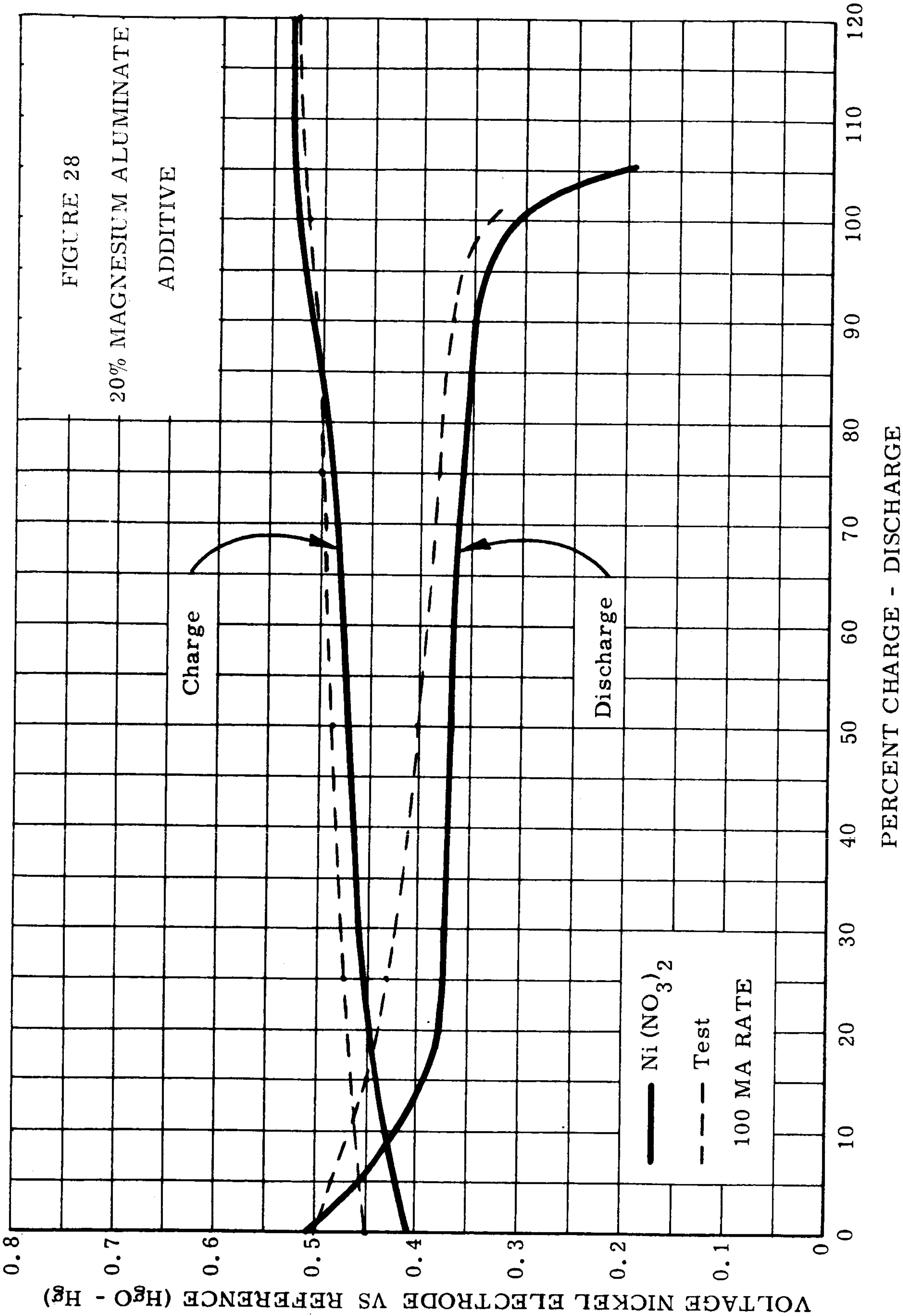

FIGURE 28
20% MAGNESIUM ALUMINATE ADDITIVE

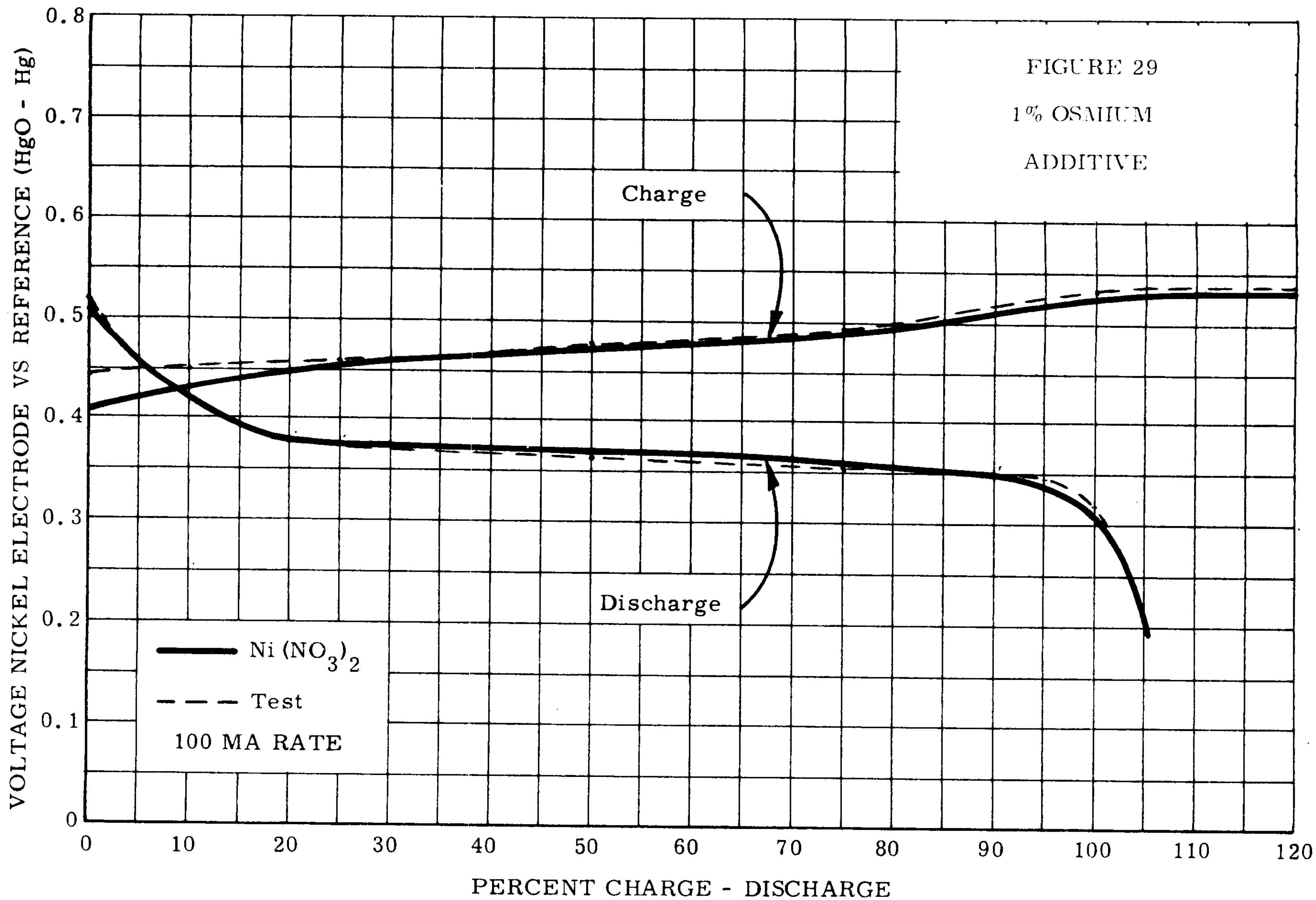
FIGURE 29
1% OSMIUM
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
PERCENT CHARGE - DISCHARGE

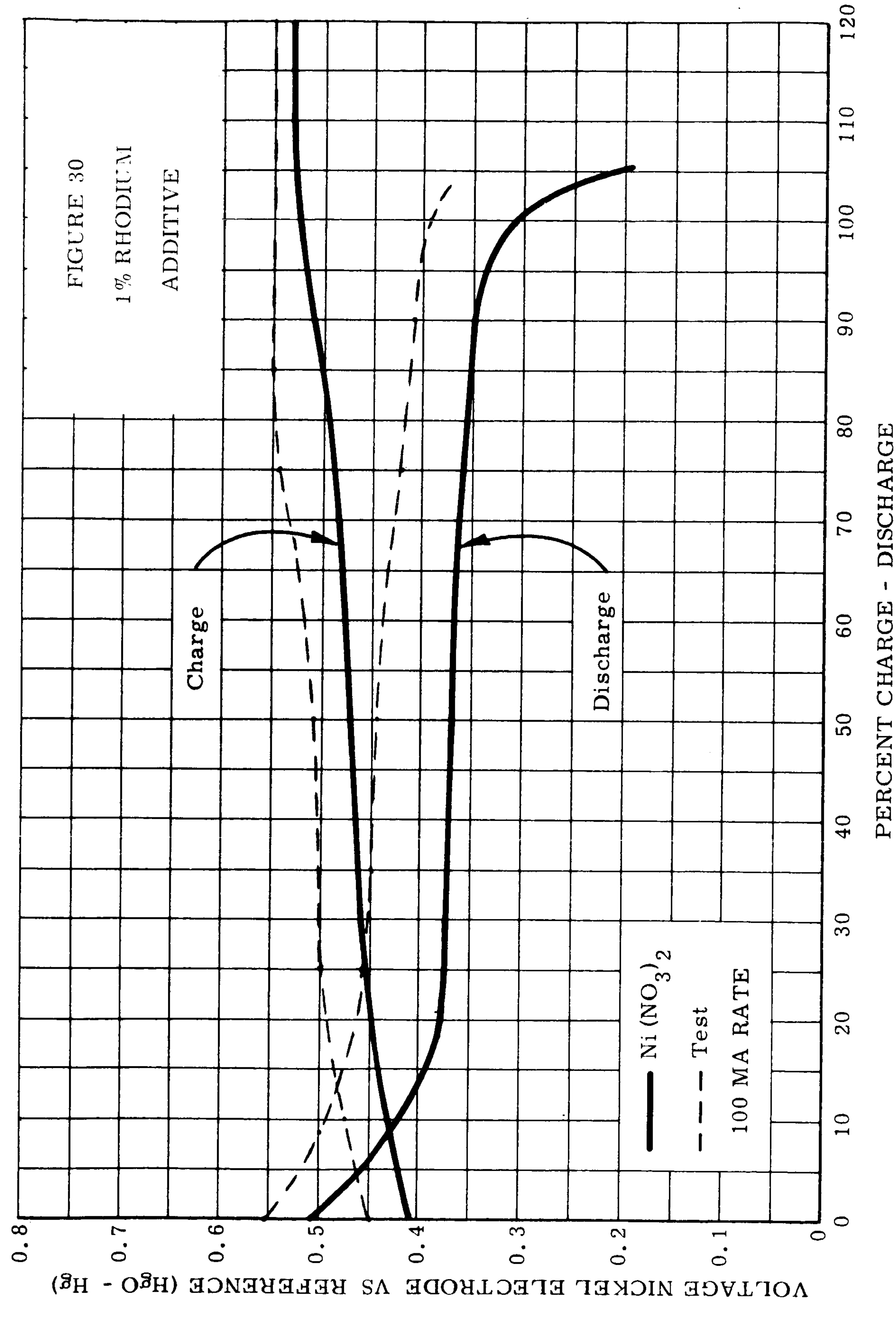

FIGURE 30
1% RHODIUM ADDITIVE

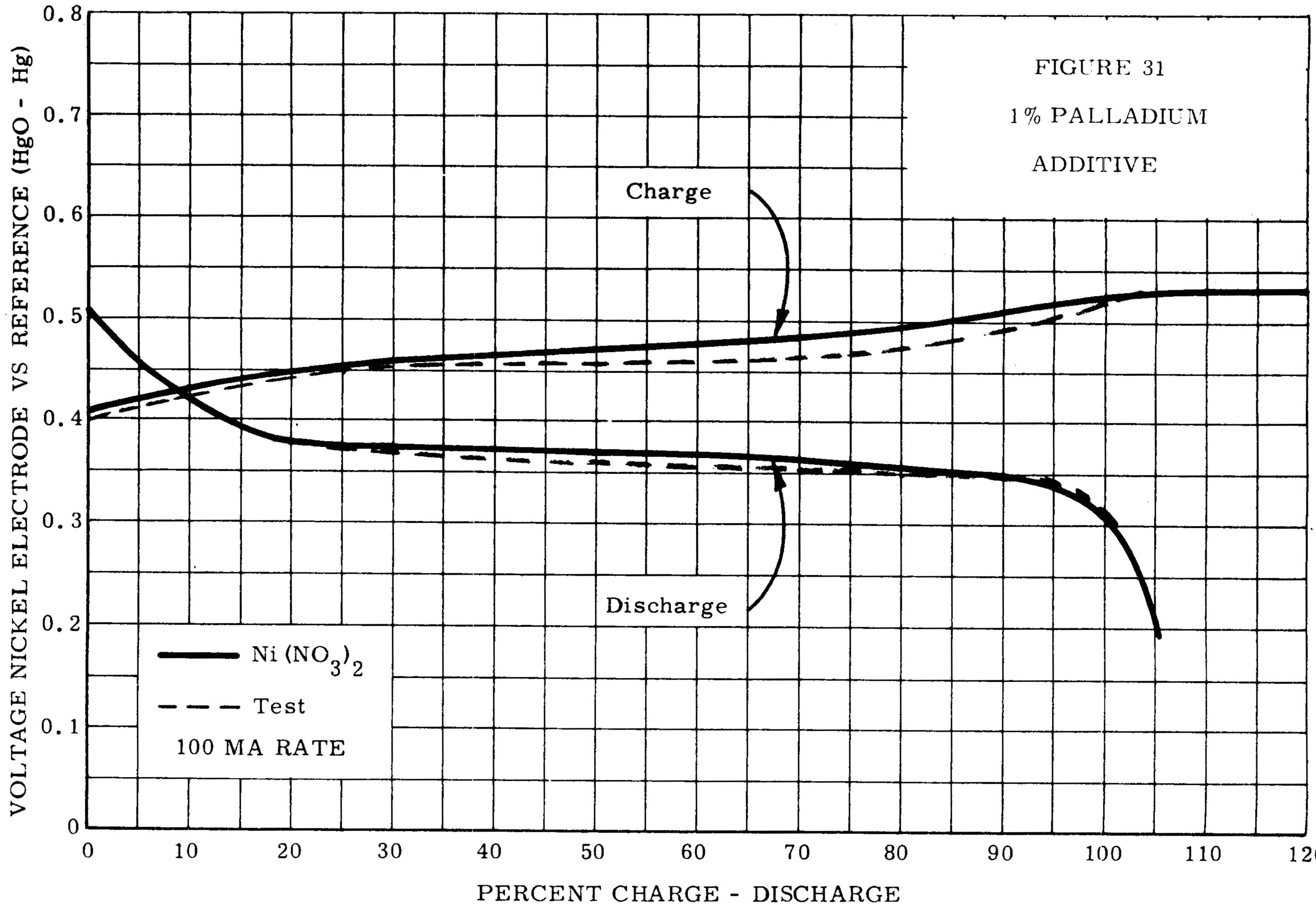
FIGURE 31
1% PALLADIUM
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
PERCENT CHARGE - DISCHARGE

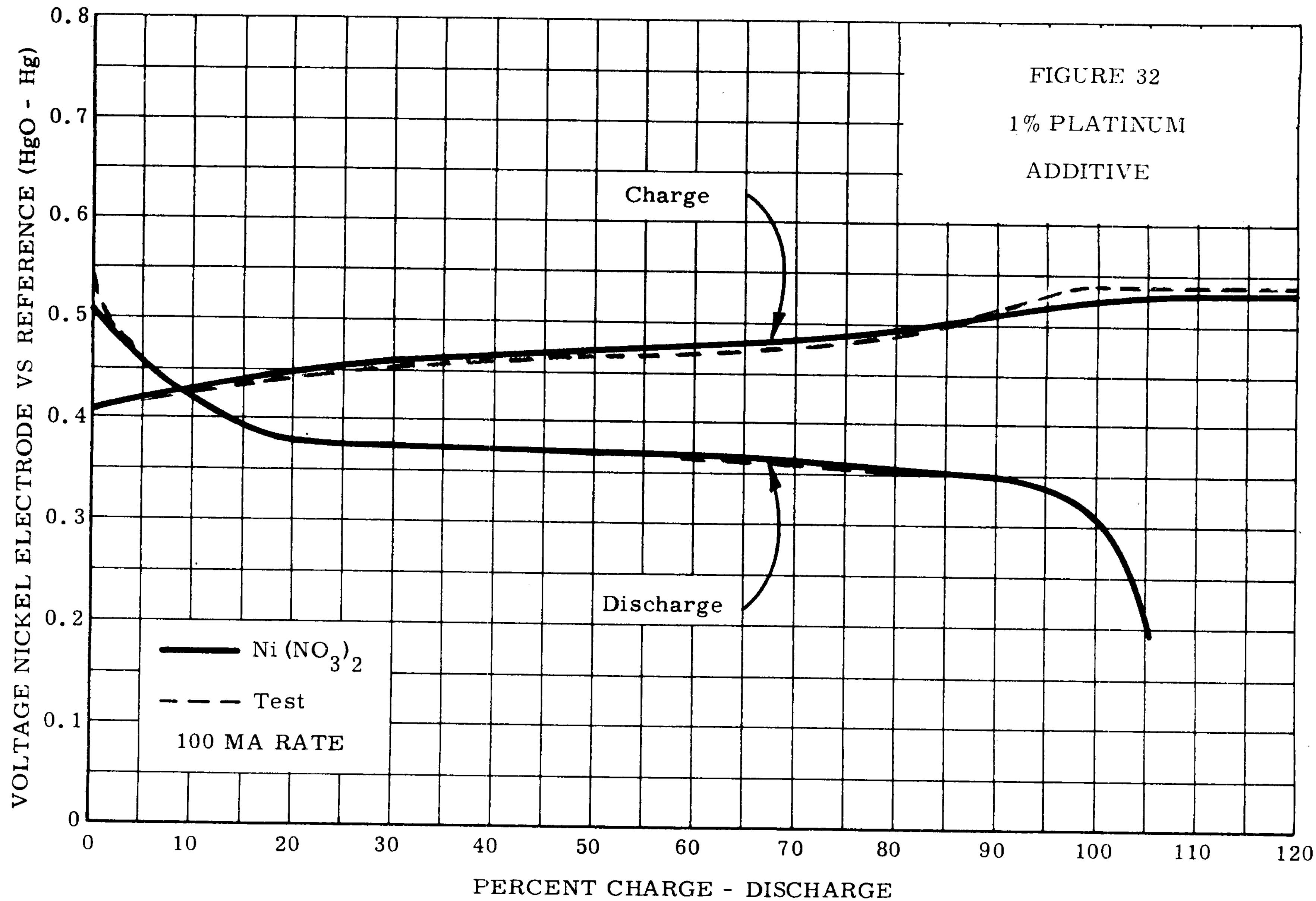
FIGURE 32
1% PLATINUM
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
10
20
30
40
50
60
70
80
90
100
110
120

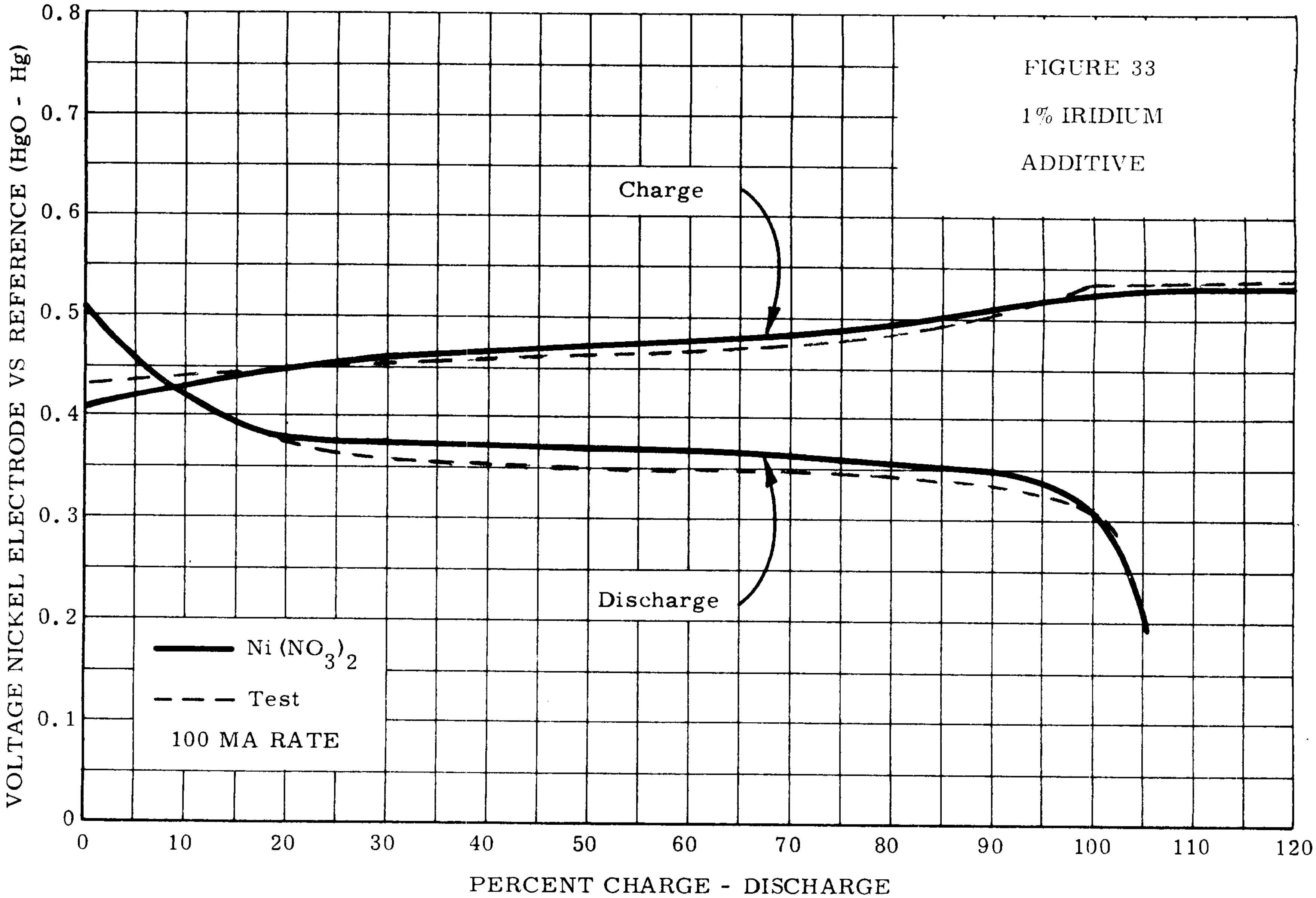
FIGURE 33
1% IRIDIUM
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
10
20
30
40
50
60
70
80
90
100
110
120

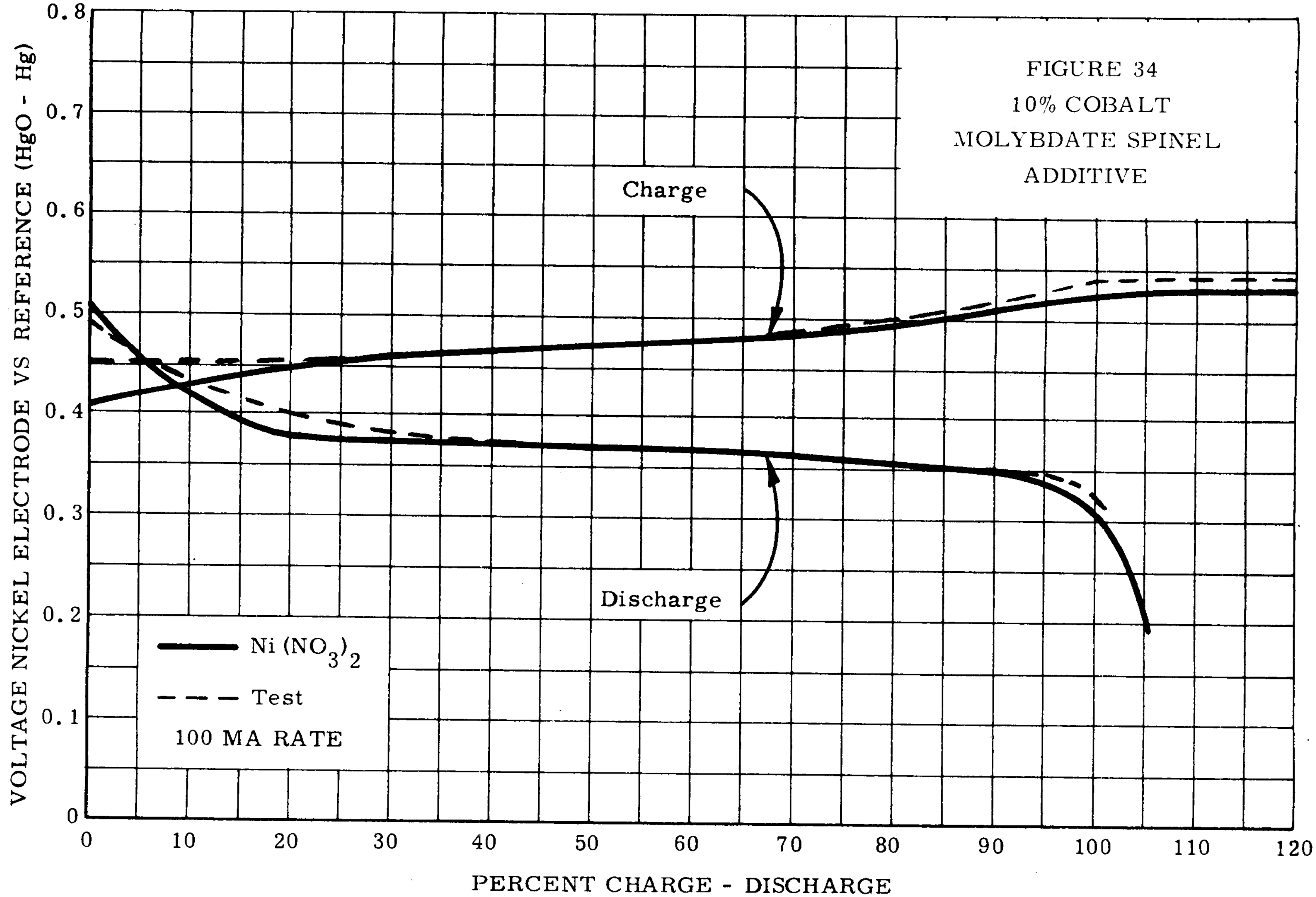
FIGURE 34
10% COBALT
MOLYBDATE SPINEL
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
10
20
30
40
50
60
70
80
90
100
110
120

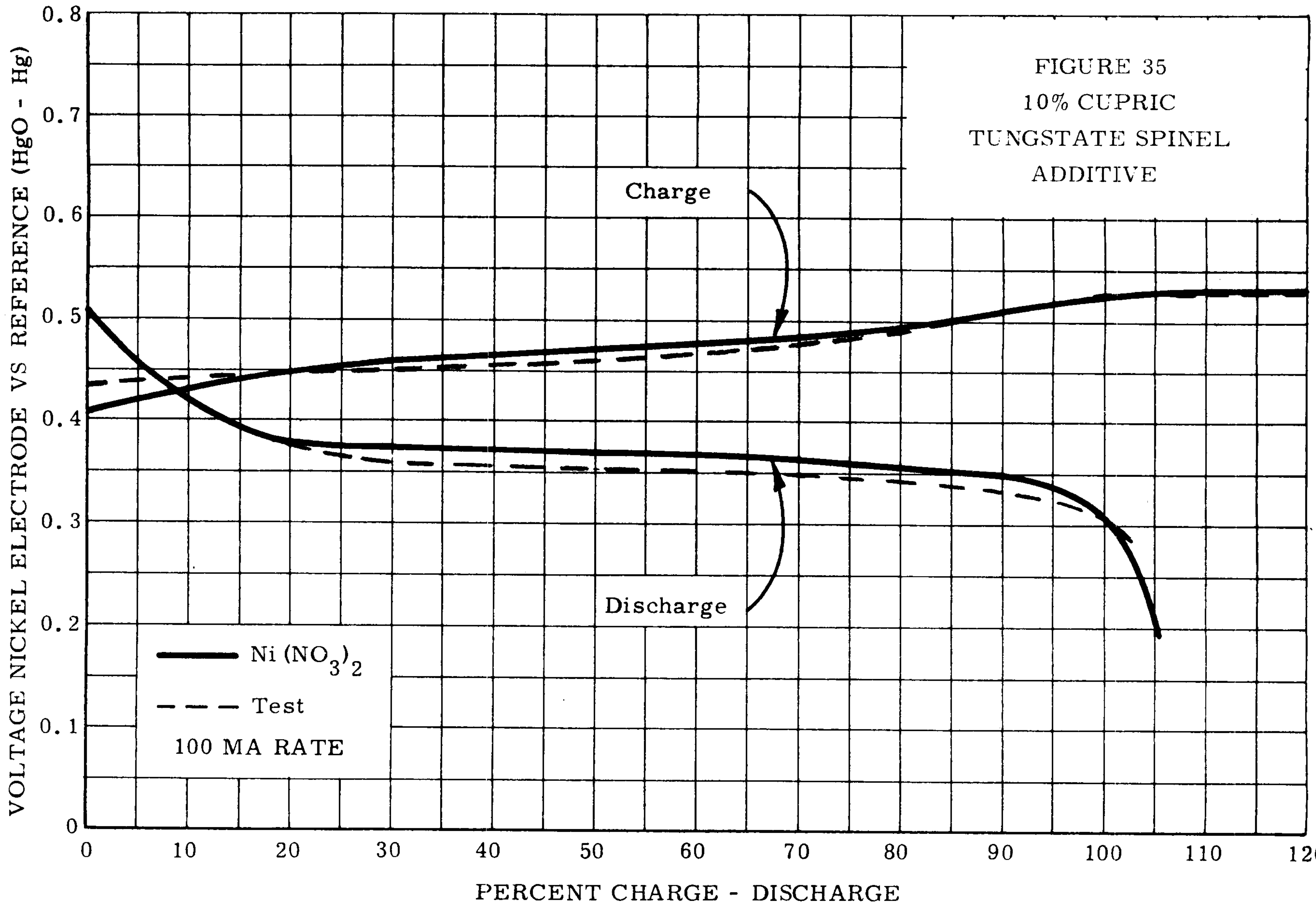

FIGURE 35
10% CUPRIC
TUNGSTATE SPINEL
ADDITIVE

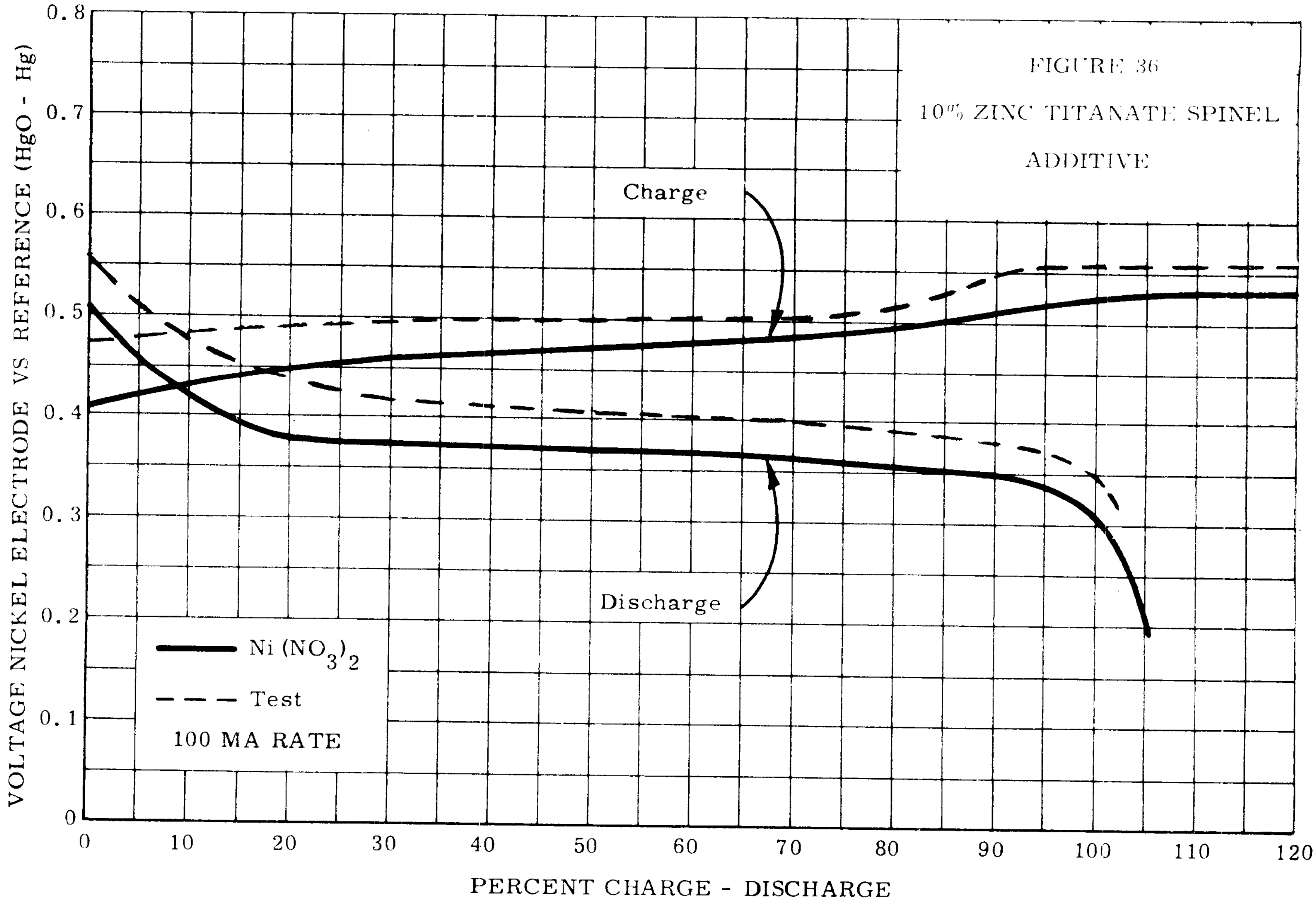

FIGURE 36
10% ZINC TITANATE SPINEL
ADDITIVE

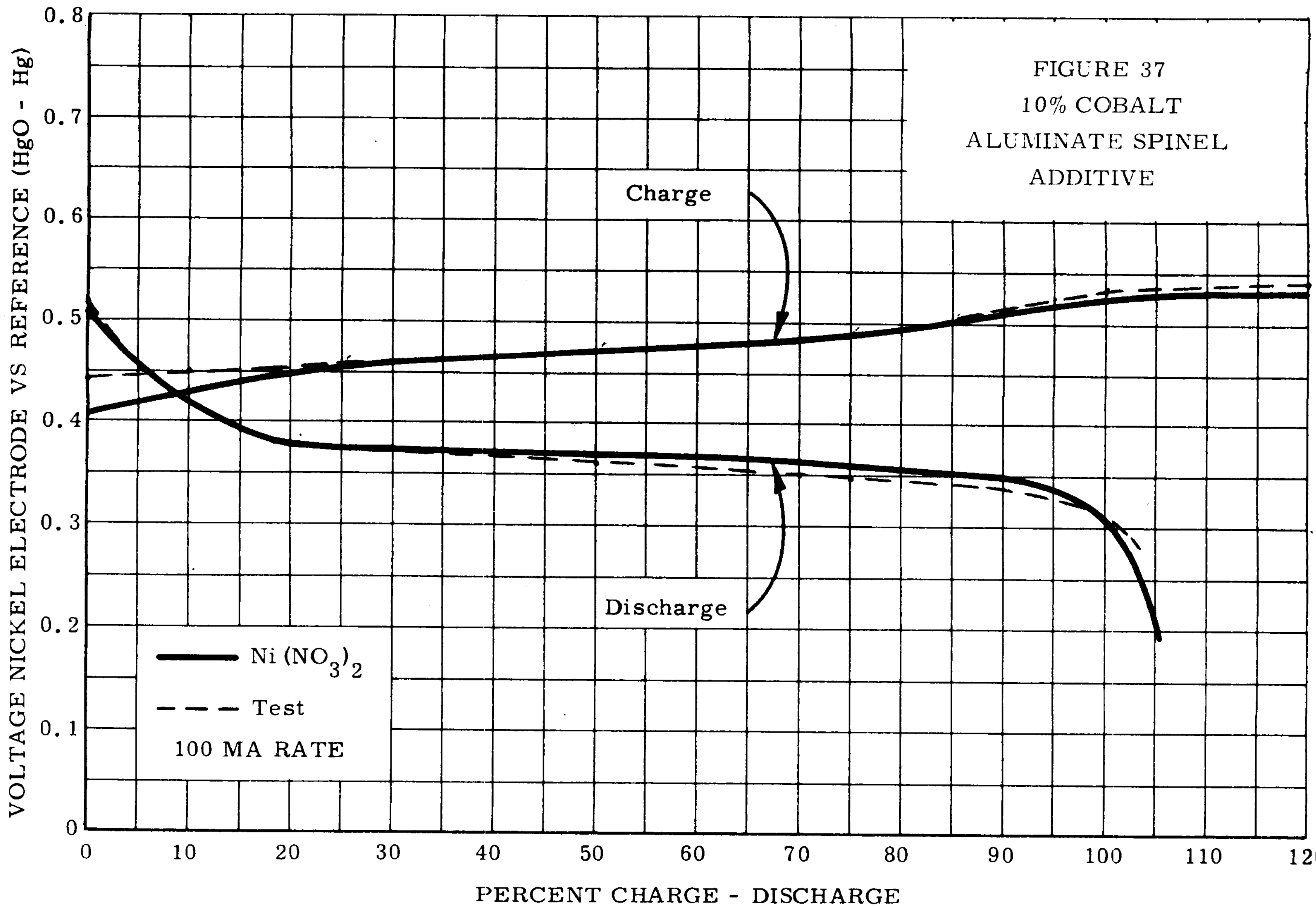

FIGURE 37
10% COBALT
ALUMINATE SPINEL
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
10
20
30
40
50
60
70
80
90
100
110
120

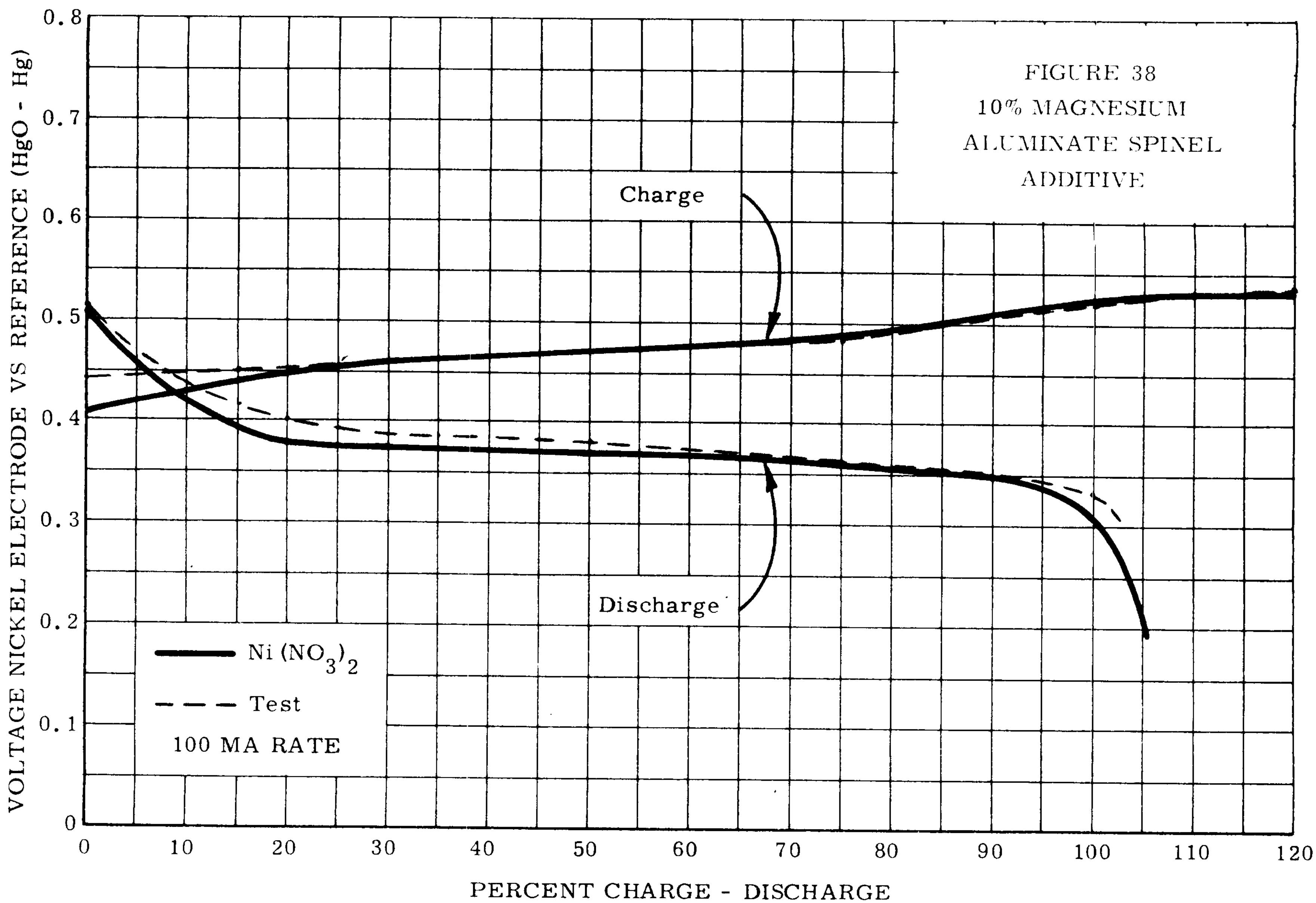

FIGURE 38
10% MAGNESIUM
ALUMINATE SPINEL
ADDITIVE
Charge
Discharge
Ni $(NO_3)_2$
Test
100 MA RATE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE

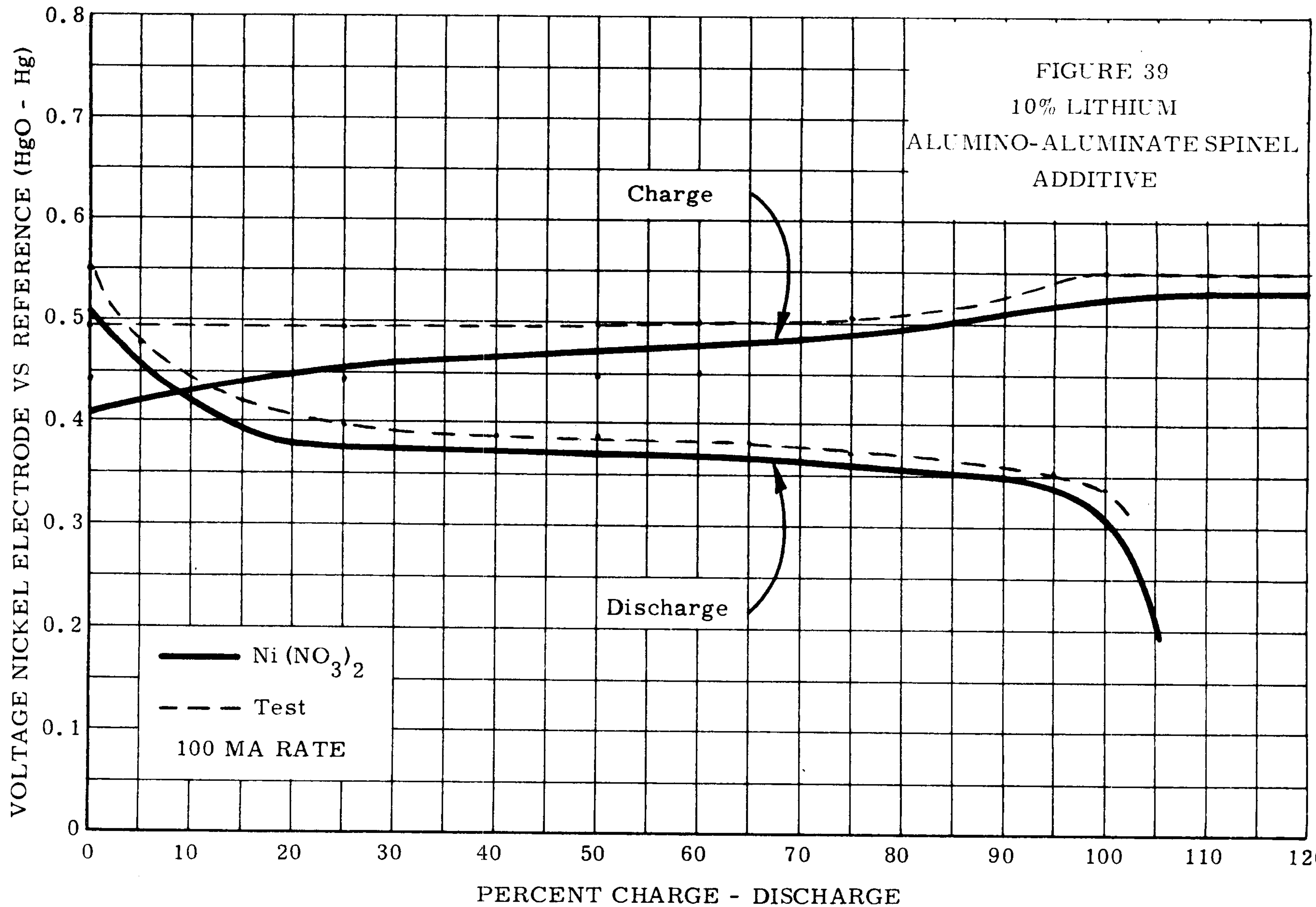
FIGURE 39
10% LITHIUM
ALUMINO-ALUMINATE SPINEL
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
10
20
30
40
50
60
70
80
90
100
110
120

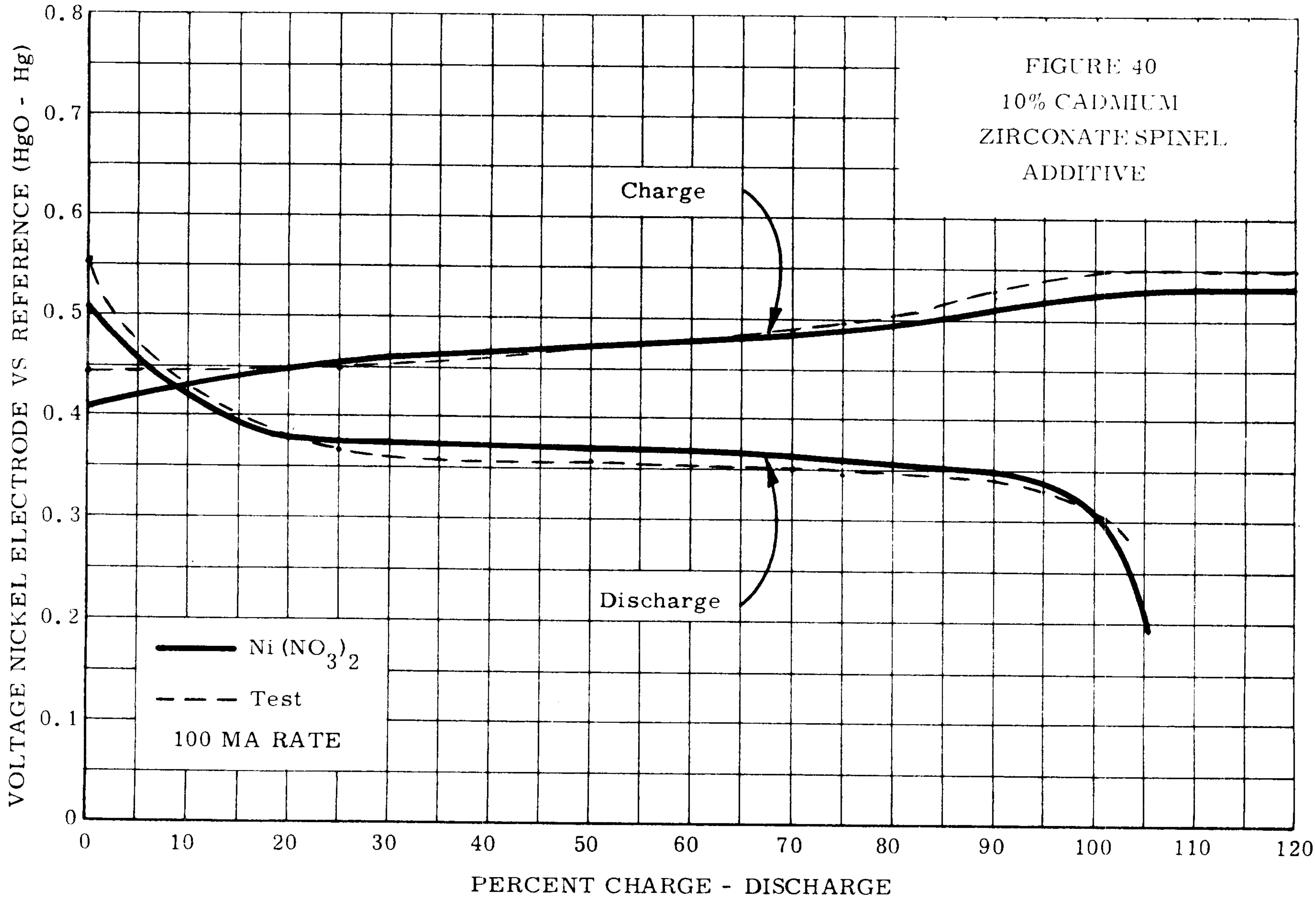

FIGURE 40
10% CADMIUM
ZIRCONATE SPINEL
ADDITIVE

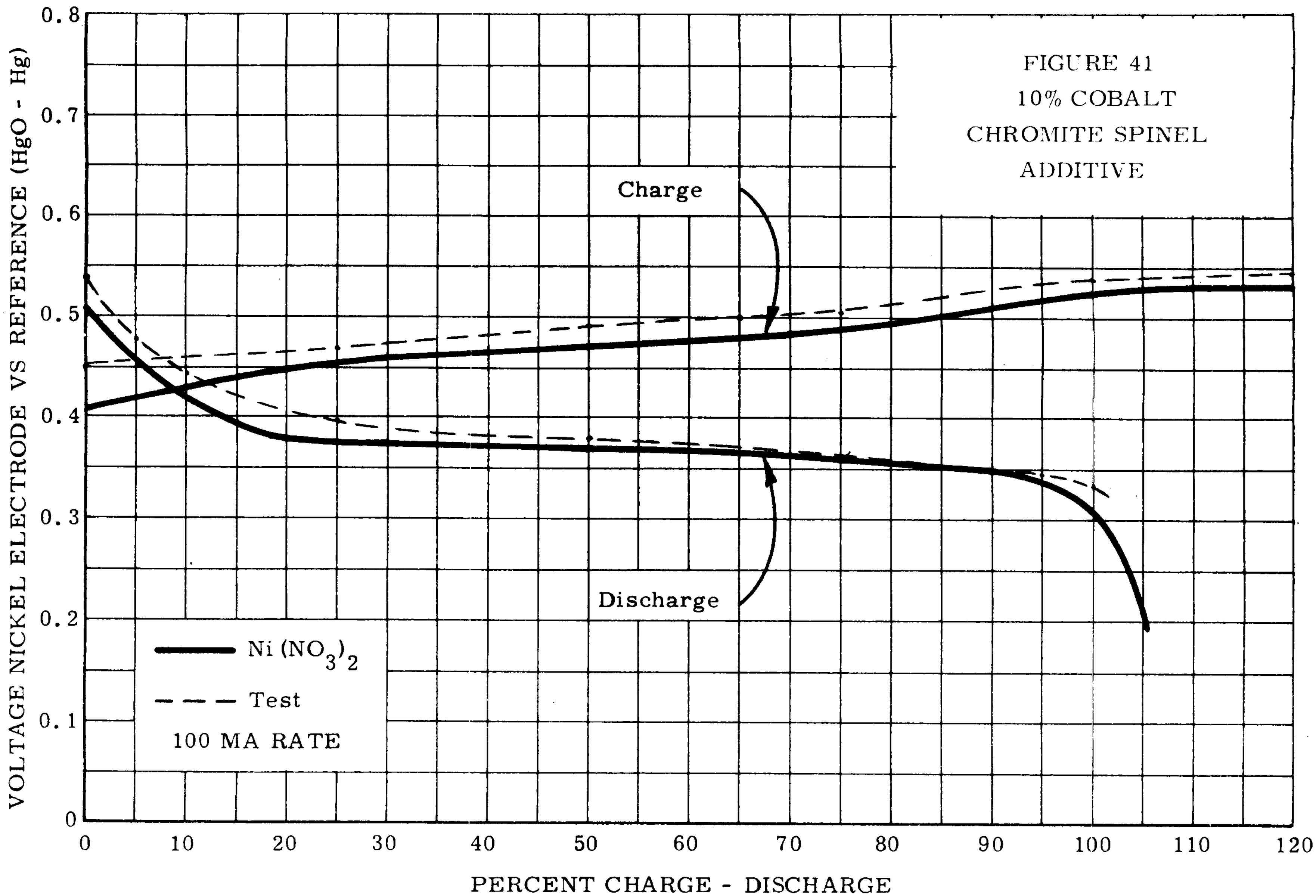
FIGURE 41
10% COBALT
CHROMITE SPINEL
ADDITIVE
Charge
Discharge
Ni (NO3)2
Test
100 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
10
20
30
40
50
60
70
80
90
100
110
120

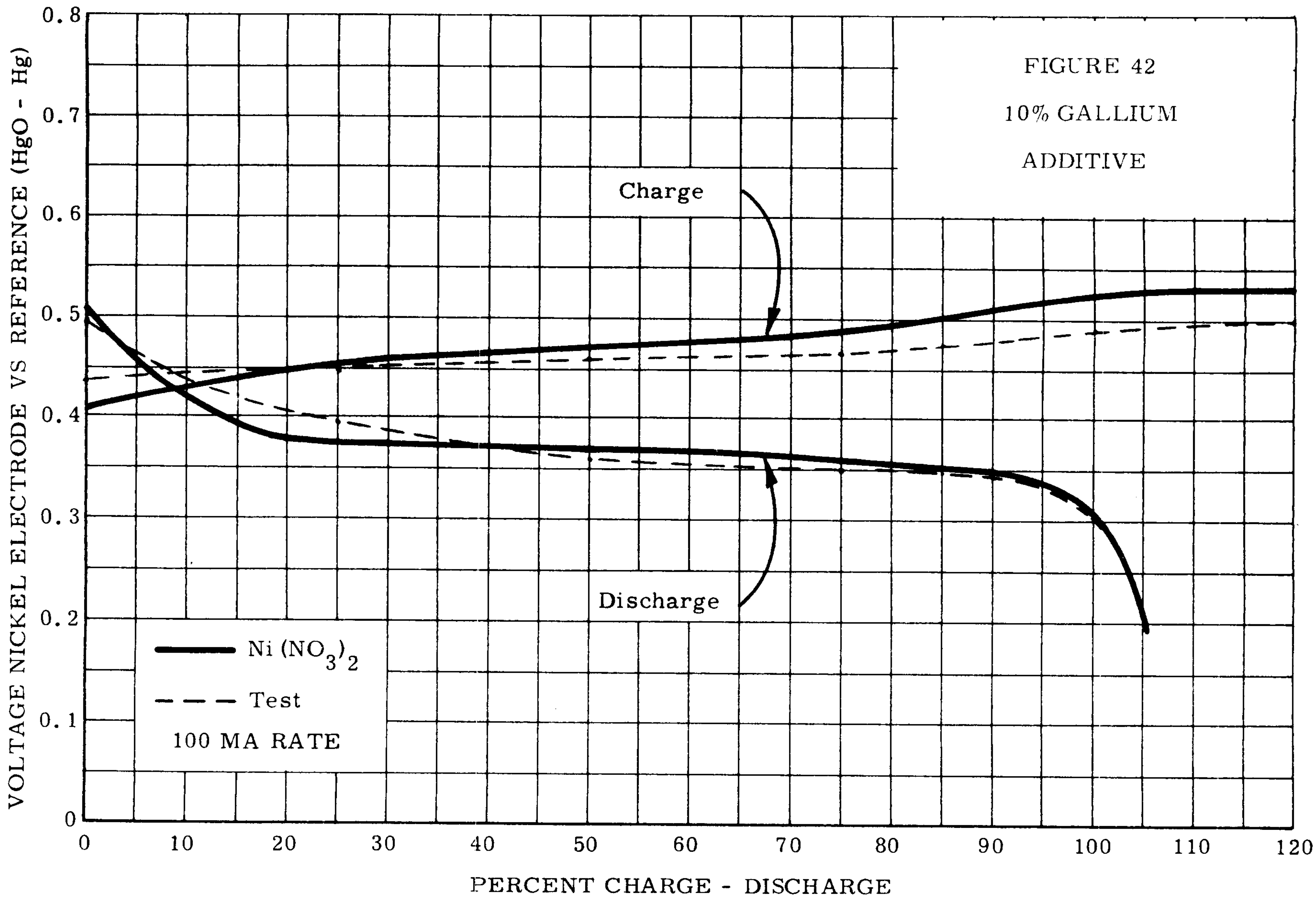
FIGURE 42
10% GALLIUM
ADDITIVE
Charge
Discharge
$Ni(NO_3)_2$
Test
100 MA RATE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE

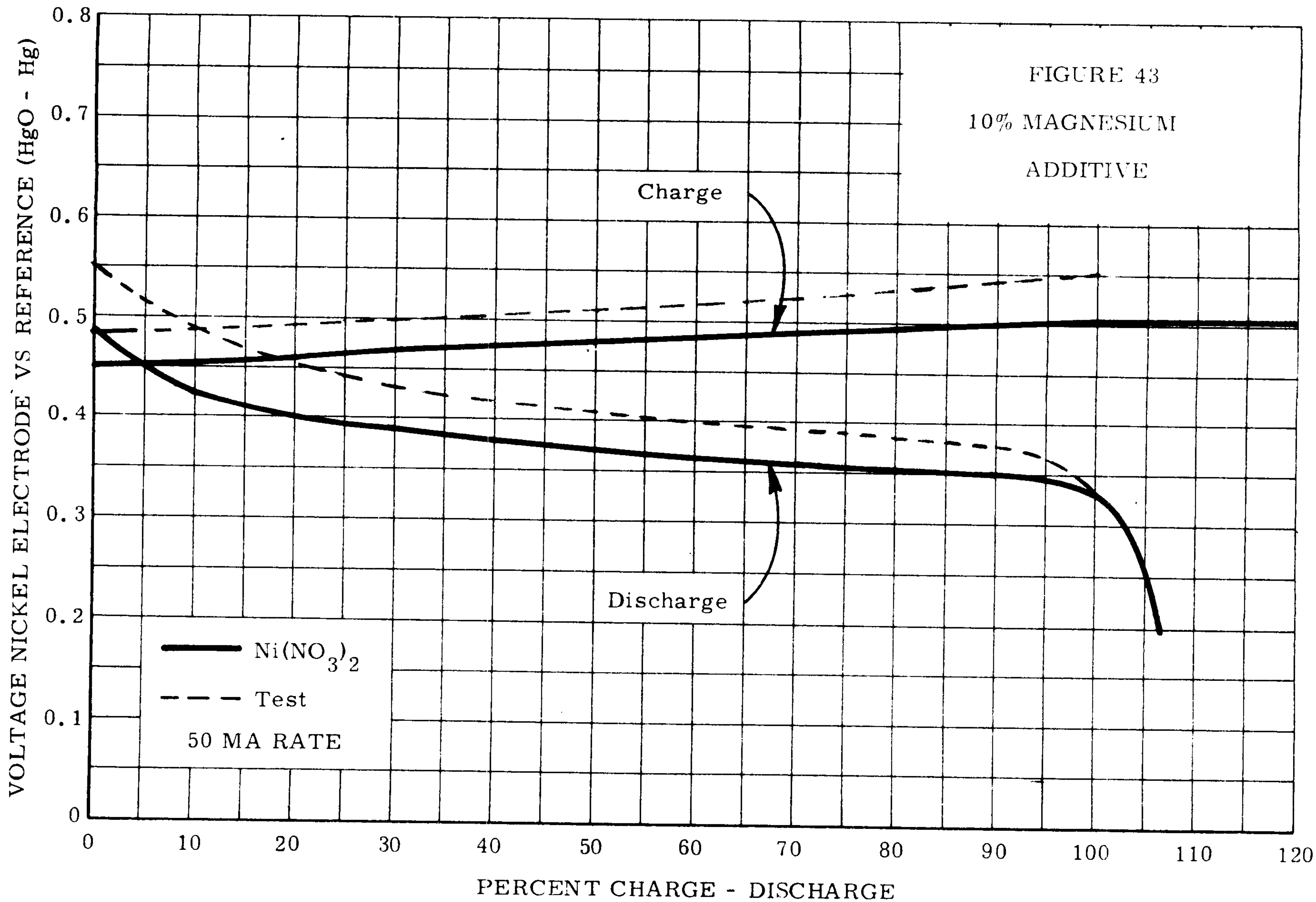

FIGURE 43
10% MAGNESIUM ADDITIVE

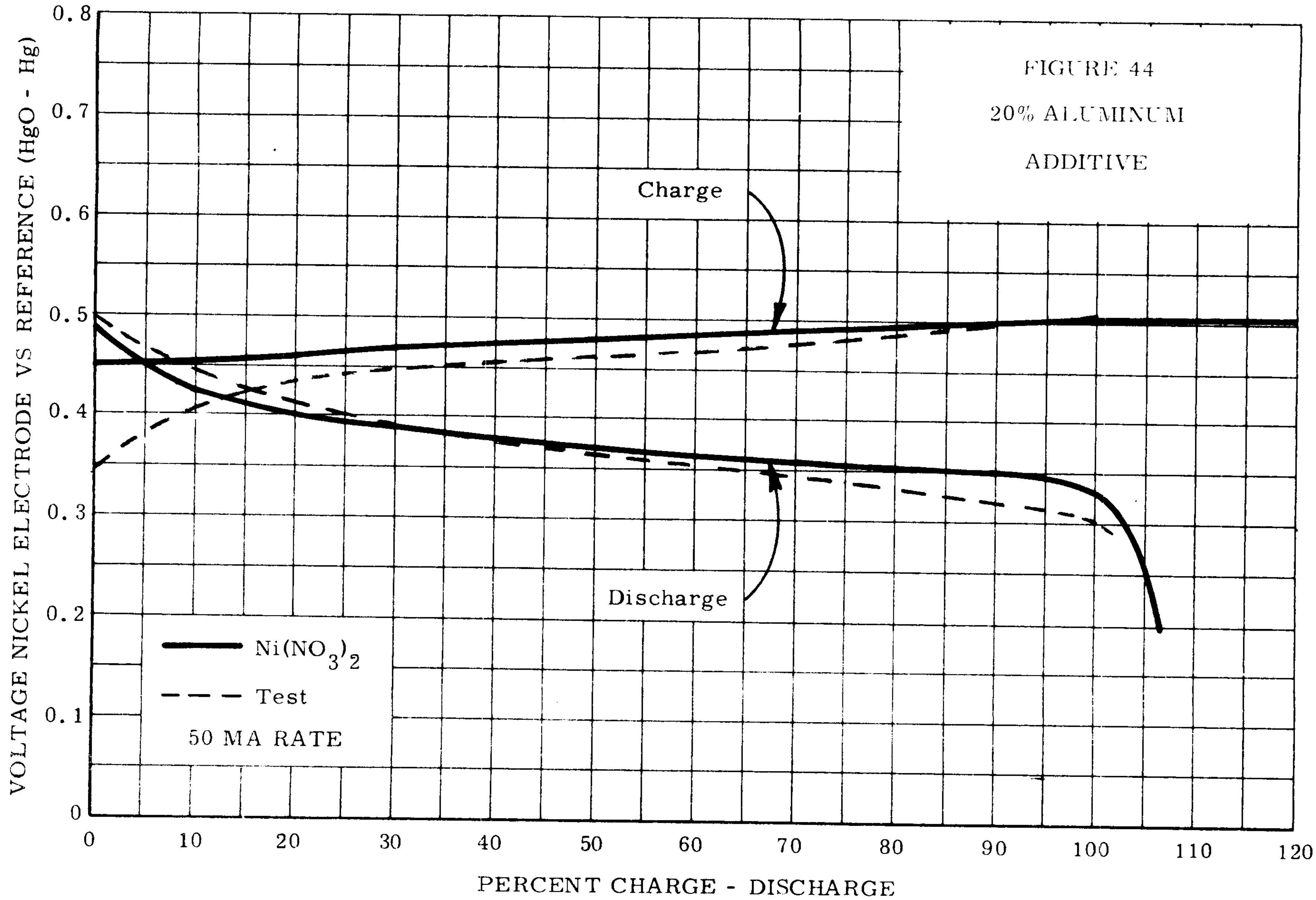
FIGURE 44
20% ALUMINUM
ADDITIVE
Charge
Discharge
Ni(NO3)2
Test
50 MA RATE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
PERCENT CHARGE - DISCHARGE

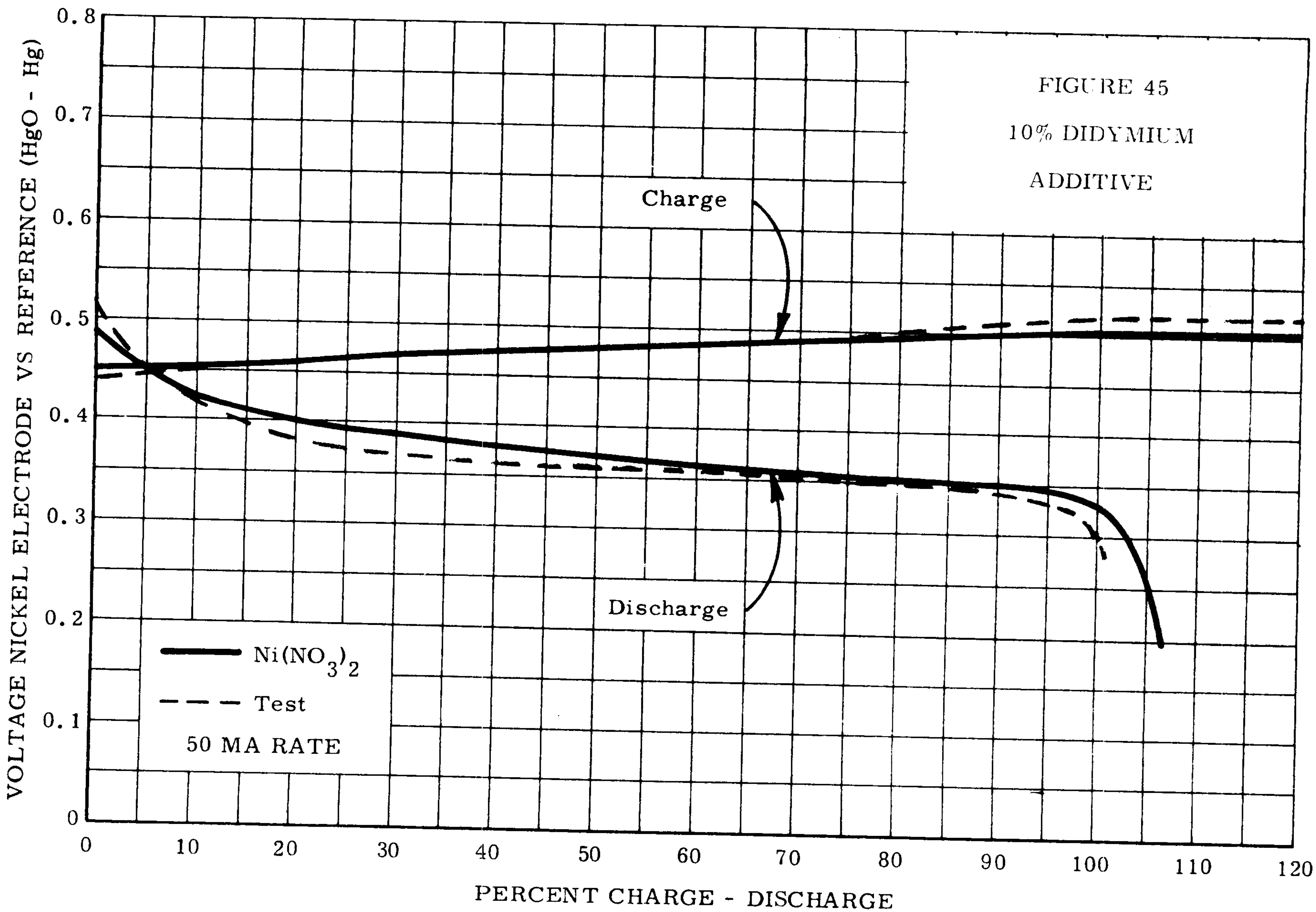
FIGURE 45
10% DIDYMIUM
ADDITIVE
Charge
Discharge
Ni(NO3)2
Test
50 MA RATE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
PERCENT CHARGE - DISCHARGE

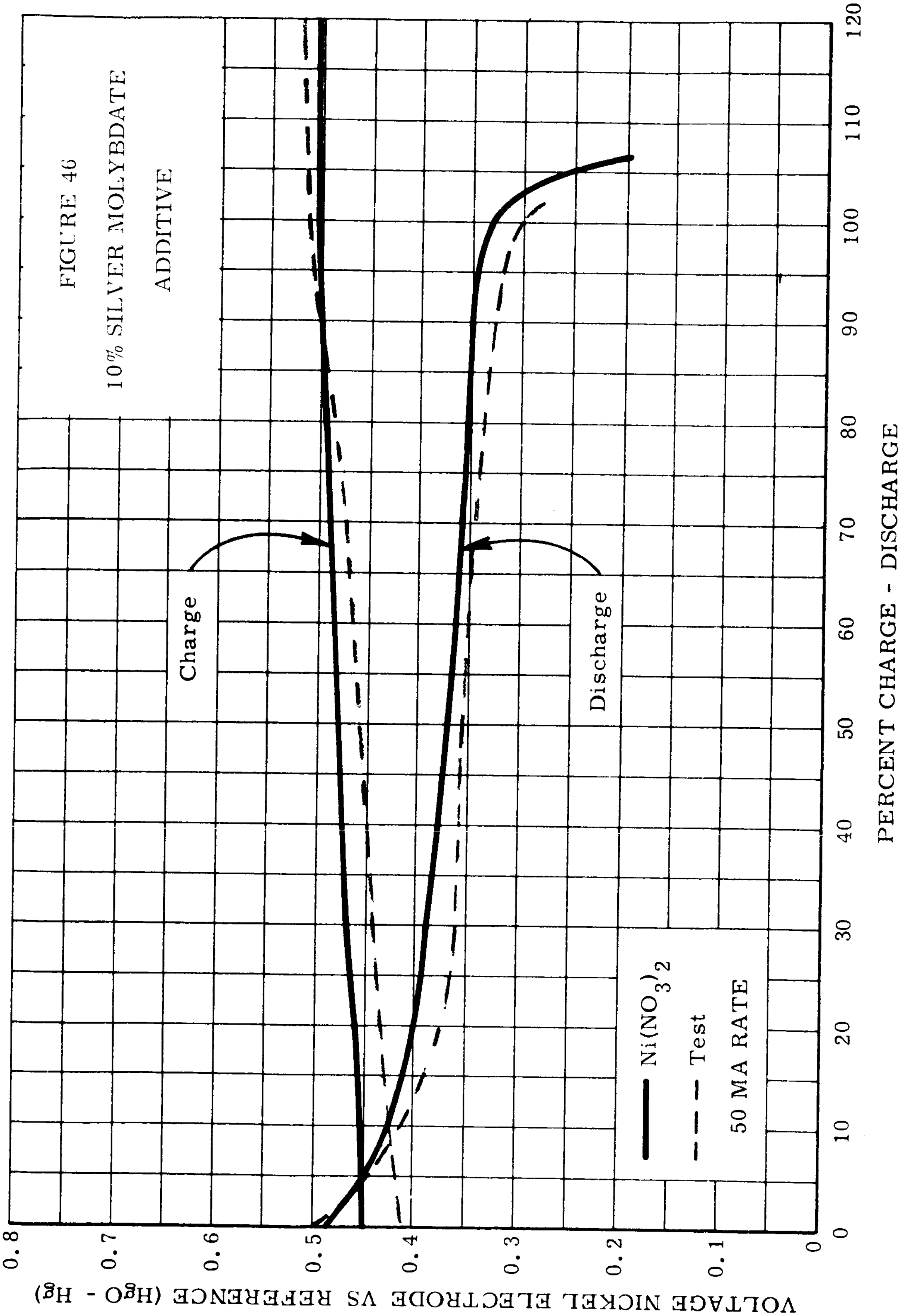

FIGURE 46
10% SILVER MOLYBDATE
ADDITIVE

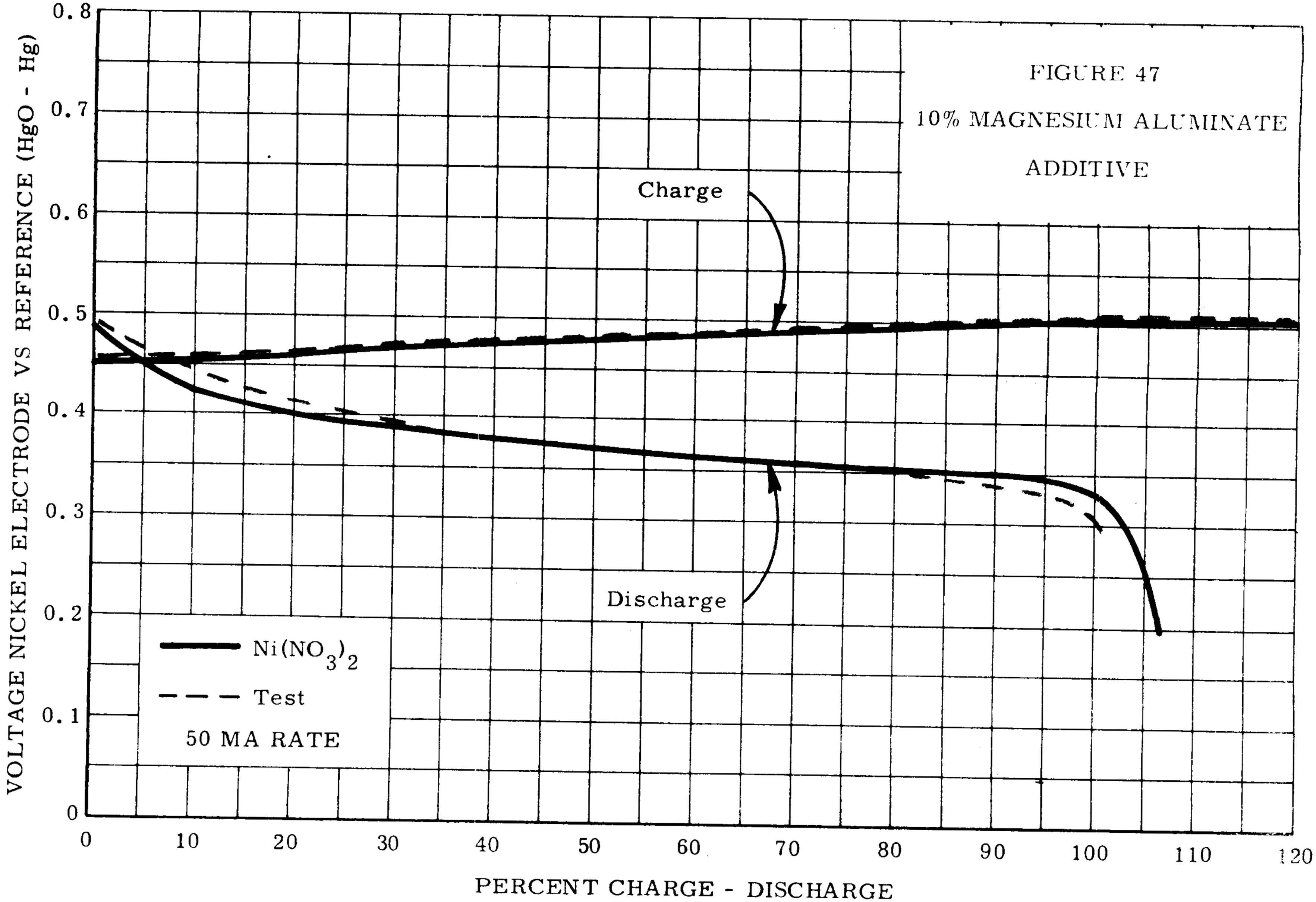

FIGURE 47
10% MAGNESIUM ALUMINATE ADDITIVE

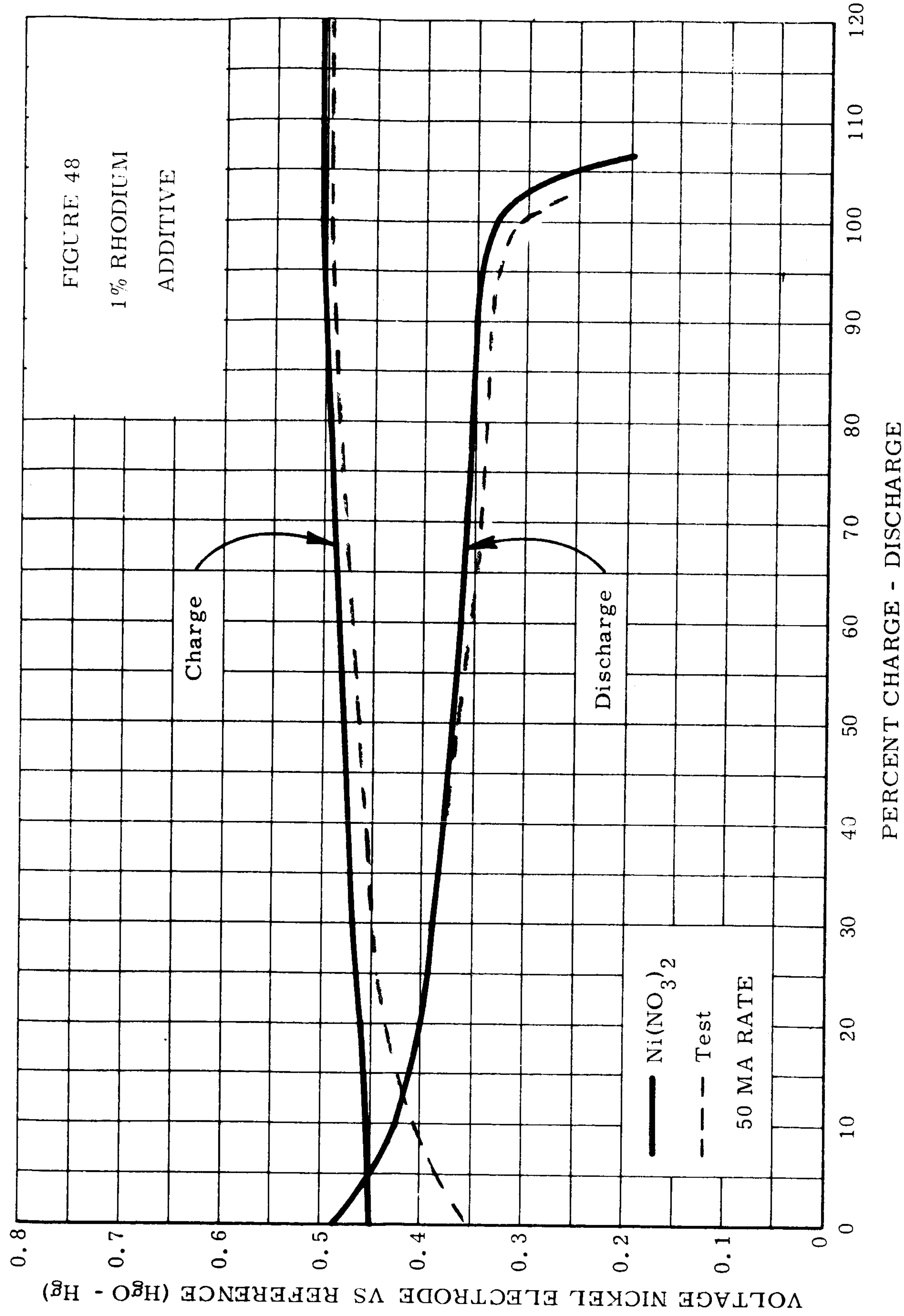

FIGURE 48
1% RHODIUM ADDITIVE

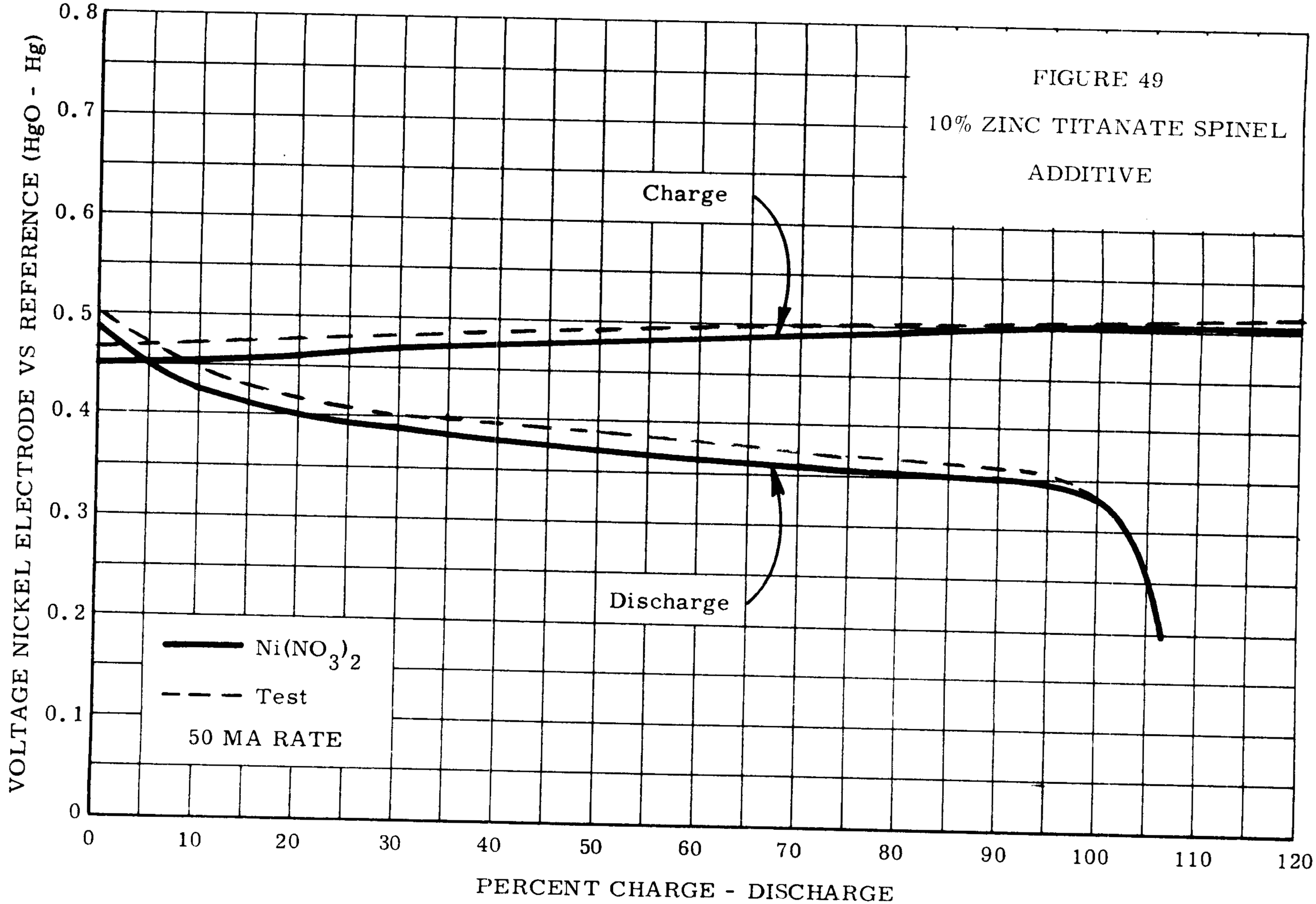

FIGURE 49
10% ZINC TITANATE SPINEL ADDITIVE

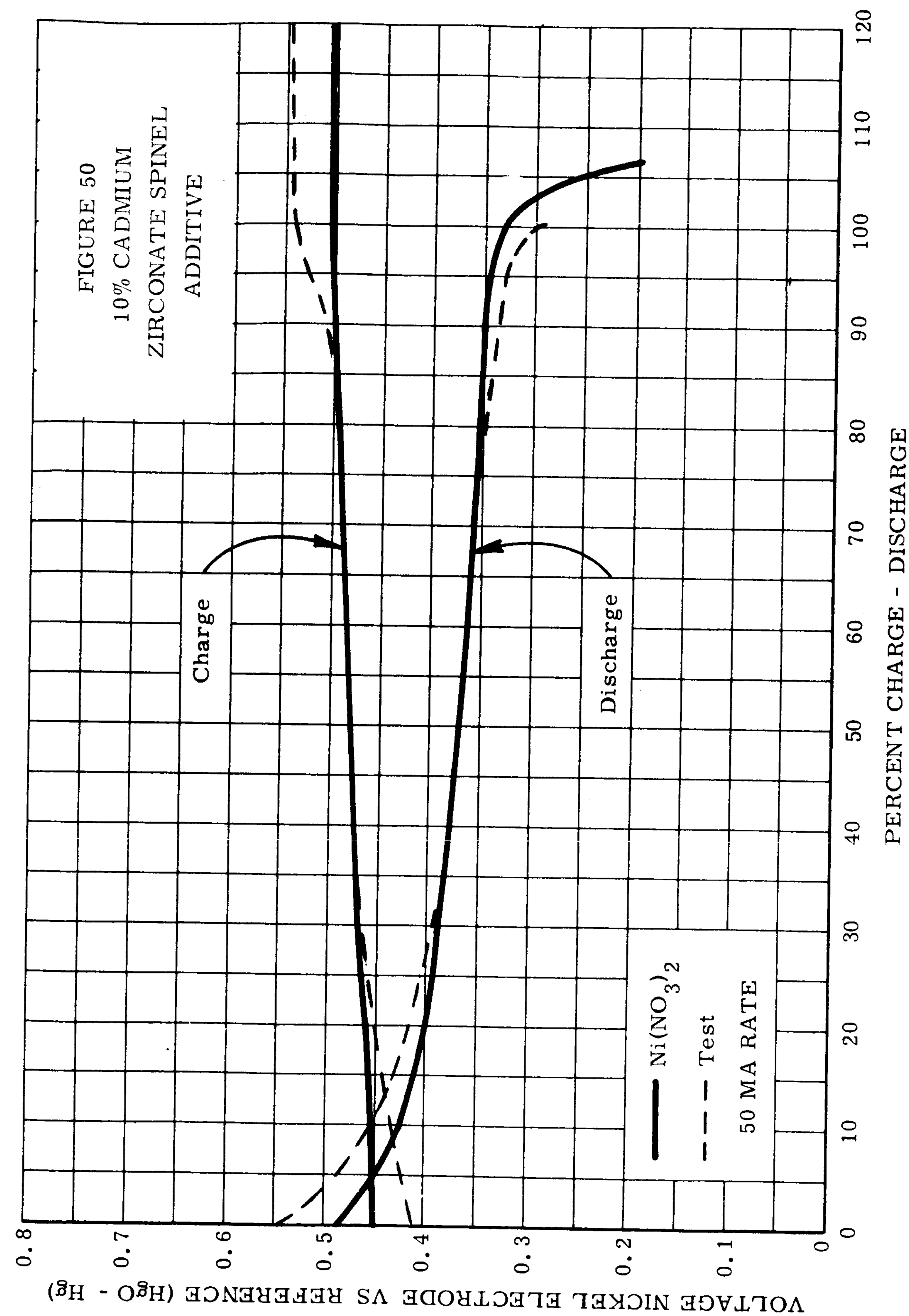

FIGURE 50
10% CADMIUM
ZIRCONATE SPINEL
ADDITIVE

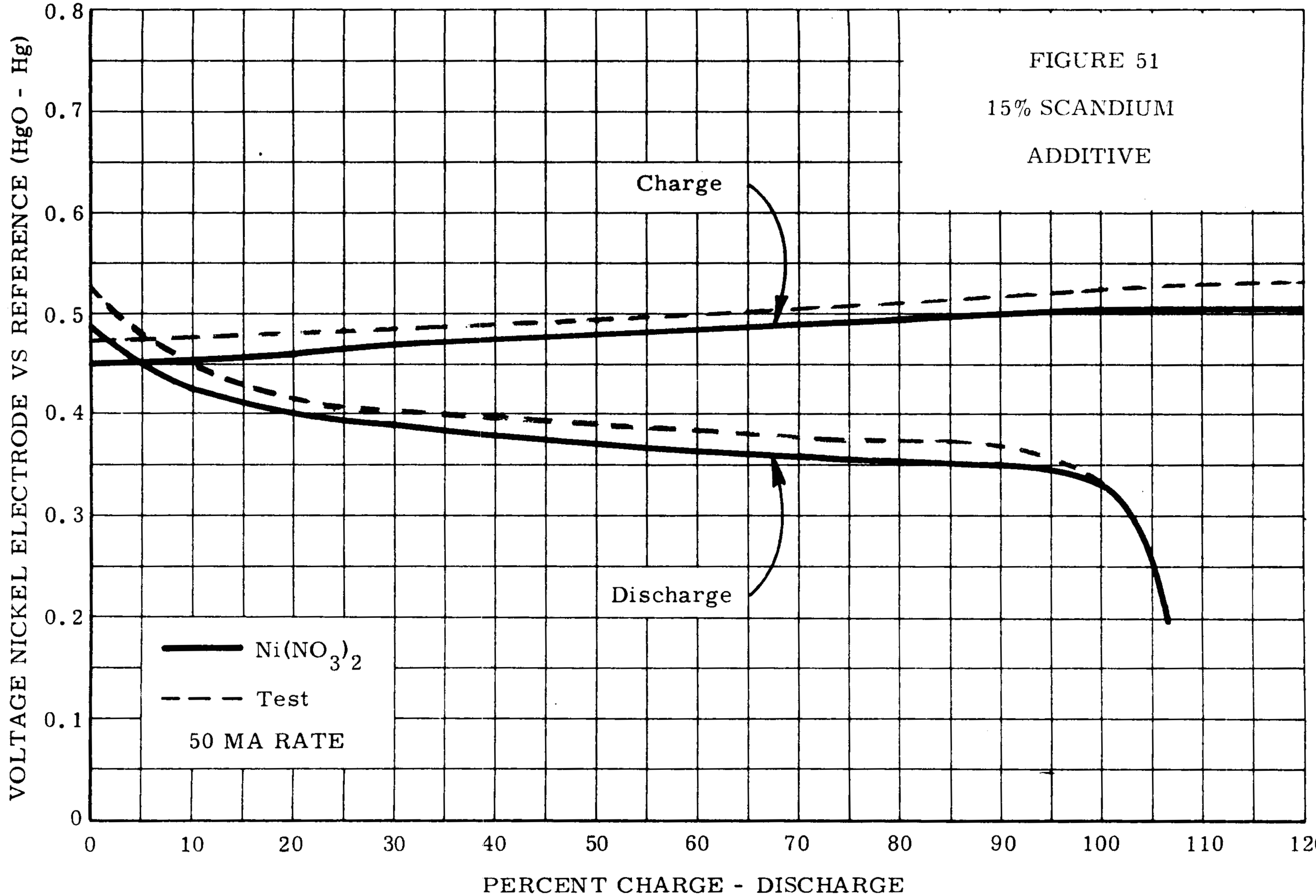

FIGURE 51
15% SCANDIUM
ADDITIVE

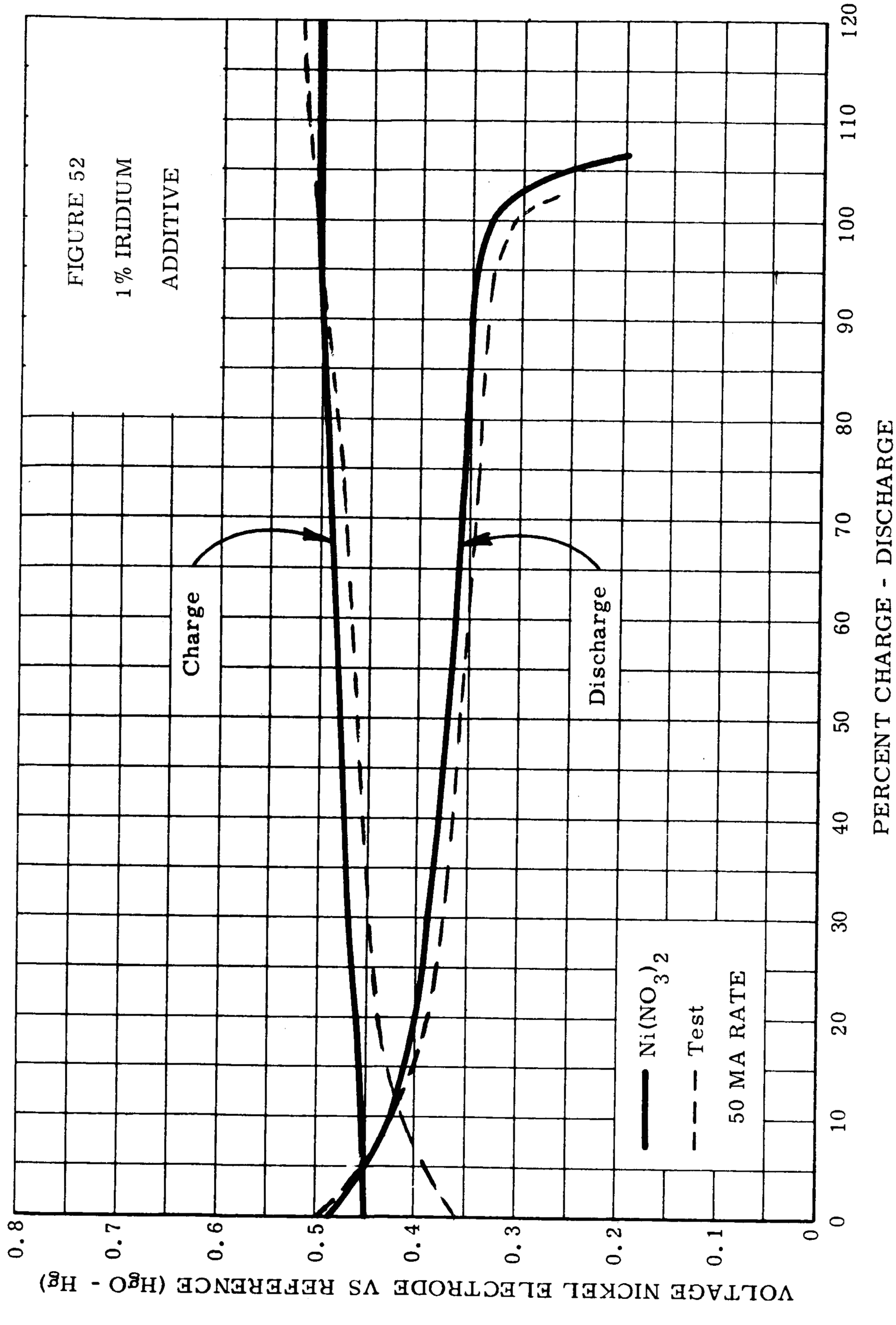
FIGURE 52
1 % IRIDIUM
ADDITIVE
Charge
Discharge
Ni(NO3)2
Test
50 MA RATE
PERCENT CHARGE - DISCHARGE
VOLTAGE NICKEL ELECTRODE VS REFERENCE (HgO - Hg)
0
10
20
30
40
50
60
70
80
90
100
110
120
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

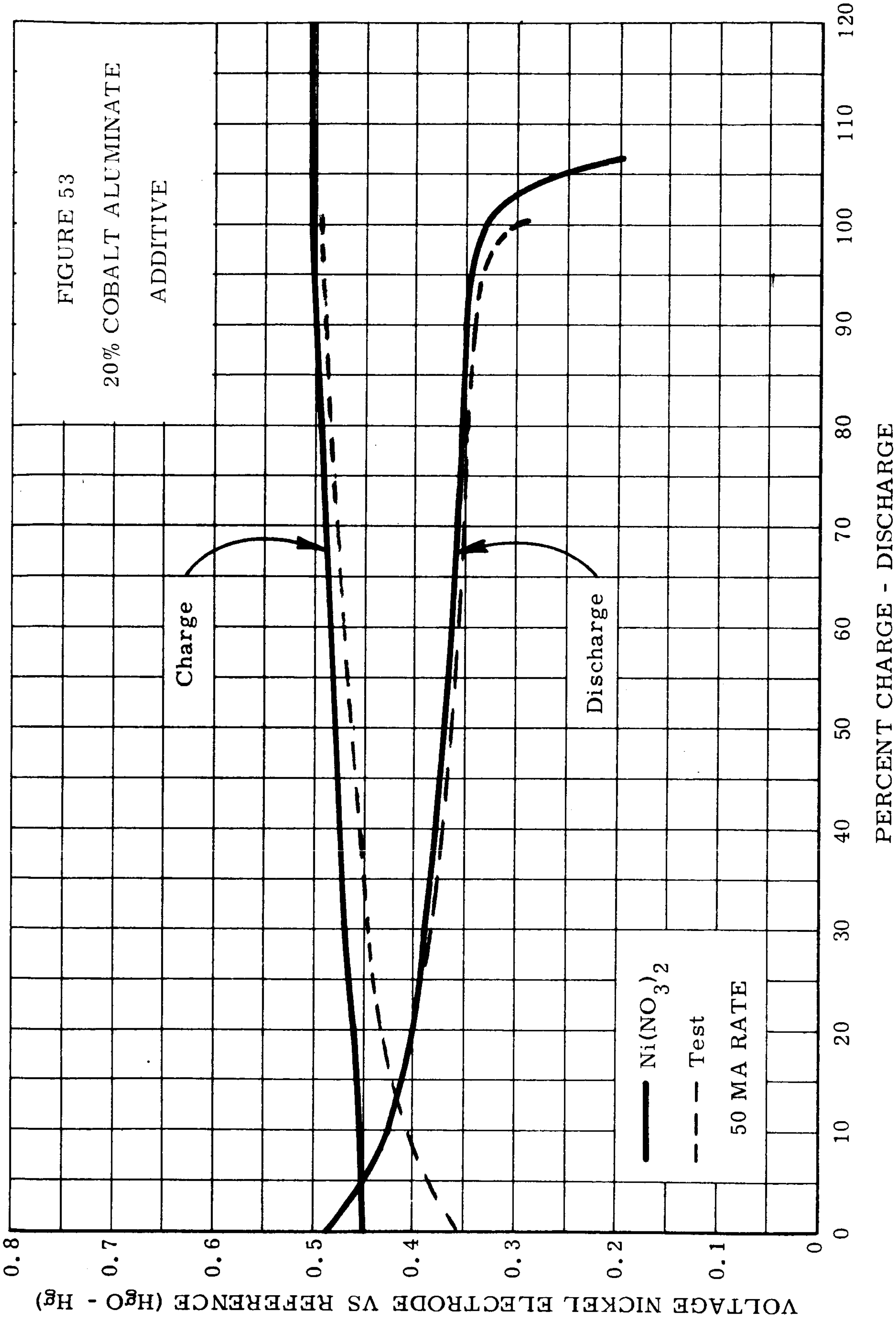

FIGURE 53
20% COBALT ALUMINATE ADDITIVE