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Sealed Lithium Inorganic Battery

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SEALED LITHIUM INORGANIC BATTERY

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Studies were continued of the effects of hardware materials on the storage and discharge characteristics of Li/$SOCl_2$ cells. Two effects were considered in particular: the ability of the hardware surface to carry the reduction of thionyl chloride when in contact with lithium (self discharge) and the corrosion of hardware materials resulting in the formation of soluble iron species and secondary iron deposits on the anode surface (anode passivation). The results are presented for 304 stainless steel showing a significant rate of self discharge due to the

reduction of thionyl chloride and an insignificant influence of the hardware corrosion on the anode passivation on storage. The tests with Kovar showed so far a negligible rate of iron generation in the electrolyte, when the Kovar hardware components are in contact with either lithium or carbon electrode. The tests in progress should show soon if Kovar is any different from the other materials in reducing thionyl chloride (self discharge) during storage at various temperatures.

TABLE OF CONTENTS

SUMMARY

Studies were continued of the effects of hardware materials on the storage and discharge characteristics of $Li/SOCl_2$ cells. Two effects were considered in particular: the ability of the hardware surface to carry the reduction of thionyl chloride when in contact with lithium (self discharge) and the corrosion of hardware materials resulting in the formation of soluble iron species and secondary iron deposits on the anode surface (anode passivation). The results are presented for 304 stainless steel showing a significant rate of self discharge due to the reduction of thionyl chloride and an insignificant influence of the hardware corrosion on the anode passivation on storage. The tests with Kovar showed so far a negligible rate of iron generation in the electrolyte, when the Kovar hardware components are in contact with either lithium or carbon electrode. The tests in progress should show soon if Kovar is any different from the other materials in reducing thionyl chloride (self discharge) during storage at various temperatures.

1. INTRODUCTION

Lithium inorganic batteries with a high discharge rate capability are now available, with an energy density higher than that of any other type of battery. The specific requirements of the US Army ECOM, however, list the high energy density as only one of the characteristics desired; it places an equal emphasis on safety in handling and use, long shelf life, and the capability of discharge at high rates. We have demonstrated in the course of the program so far that energy densities in excess of 200 Wh/lb and 15 Wh/in^3 could be achieved with ease, particularly since the computer aided cell design was introduced. Further efforts in this direction could not be justified at this time, at least not before a need was expressed for large quantities of these cells, and before some progress was made in the area of safe handling.

The hermeticity of the cell has been achieved with the introduction of glass-to-metal seals and appropriate welding techniques. A total absence of gas generation on storage and on discharge at low and moderate rates made possible the construction of hermetic cells without the danger of the internal pressure build up. A recent development in the assemblage techniques proved that it was feasible to use several different welding procedures and all yield satisfactory seals.

The question of safety in handling has received much attention in the last year. We have demonstrated that the thermal runaway on short circuit could be avoided in most practical situations by a fuse, by a vent or by a combination of both of these devices. In fact, the entire problem has been reduced to making a compromise between the cost of production of cells and the degree of protection afforded. The study of the thermal effects of discharge at high rates (1) revealed that there is a limiting rate for each cell size below which a steady state is reached, i.e., when the rate of heat generation is balanced with the cooling rate at a temperature below critical. A continuous rise in temperature will occur through the entire discharge period at rates higher than the limiting one, and the thermal runaway point may or may not be reached depending on the energy available in the cell to support the discharge. The safest way to limit the maximum discharge rate is to construct the electrode structure in such a way that it is incapable of delivering the energy at a rate higher than the critical one for each particular size of cell. We have demonstrated this mode of protection by producing cells of various sizes and capacities up to 30 Ah. These cells could be short circuited and would show some increase in temperature, but they reach the end of discharge long before their temperature approaches any of the possible critical points. It is quite possible that such cells may not be capable of delivering the power required by the Army's communication equipment, in which case the high rate cell construction must be employed with some appropriate protective devices.

Having achieved the desired energy density and cell hermeticity and having defined the alternatives leading to the construction of safe high rate cells, work on this project was concentrated on the remaining problems, such as the interaction of hardware corrosion, anode passivation and the rate of self discharge that results from the use of various materials in contact with cell electrodes. This latter was the main area of concern during the past several months of the program. A part of this work has been reported in the last quarter, describing the influence of cold rolled steel hardware on the performance characteristics of these cells. In the quarter covered by the present report attention was focused on the use of stainless steel as the hardware material. This material was studied in two roles: as the source of iron ions formed by corrosion, and also as an active electrode carrying the reduction of $SOCl_2$ when in contact with the anode. The details of these studies are discussed below, followed by the discussion of the preliminary results obtained with other hardware materials such as Kovar.

2. CORROSION OF STAINLESS STEEL HARDWARE

The experiments conducted in a glass cell described earlier (2) showed that the cathodic protection of cell hardware in contact with the anode may be affected by the geometry of the cell interior. We have found that a large cold rolled steel anode, with a piece of lithium attached at one end, will show visible signs of corrosion at its other end, when kept in an $SOCl_2$ electrolyte at 72°C. A series of experiments with D size cans was conducted for the purpose of demonstrating whether the relative magnitude of the can interior that is not covered by lithium would affect the amount of iron in the electrolyte generated by corrosion. The experiments included the three different arrangements one could have, with the can attached to the cathode, to the anode or unattached (floating can). It was assumed that the can interior could be effectively covered with the solid lithium foil, so it was necessary to investigate various ratios of covered and bare surfaces. With cathodes, however, one had to assume the exposure of the total can interior to the electrolyte, due to the high porosity of cathode materials.

2.1 EXPERIMENTAL AND RESULTS

Sections of various sizes of the can interior were covered with lithium using 0.5 in., 1 in., and 1.5 in. wide foils, by rolling the foil against the can wall. The effectiveness of coverage by lithium was tested by attempting to peel off the lithium layer. A good bonding of lithium to the clean surface of a stainless steel can was achieved, since one could only remove lithium from the rolled composite by cutting it in small sections and removing the sections one at a time. The can bottom and walls uncovered by lithium were exposed to the electrolyte during the tests. Following were the relative surface areas involved:

COVERAGE BY LITHIUM (Height, inches)	EXPOSED CAN AREA cm^2
0	58.65
0.5	45.98
1.0	33.31
1.5	20.64

The cans with various coverage by lithium of the interior were filled with the electrolyte to the height of 2 inches. The electrolyte volume was 38.0 cm^3 maximum, and only slightly lower for the cans with more lithium, since a thin foil (0.010 in.) was used in the rolling operation. The cans were stored at 72°C and the electrolyte was analyzed for iron after one week, two weeks and four weeks of storage. Lithium was allowed to react with water and the resultant solution was acidified with HCl before it was also analyzed for iron by Atomic Absorption (Perkin Elmer Model 460). A control analysis was run on a blank made of lithium (3.5 x 1.5 x 0.010 in.) rolled into a can, allowed to react with water immediately thereafter and subjected to the same analytical procedure. A total of 0.023 mg of iron was found in the solution. The data obtained are shown in Table 1.

The experiments involving the cathode attached to the can were carried out in an arrangement similar to that used with lithium. A single layer of porous cathode, 0.034 in. thick, was placed against the interior of the cell can with the cathode current collector welded to the can wall. Three different cathode sizes were used, 0.5, 1.0 and 1.5 in. wide in the can filled with the same amount of electrolyte as in the preceding tests. All cans were stored at 72°C and the electrolyte was analyzed for iron after 1 week, 2 weeks and 4 weeks of storage. The results obtained are summarized in Table 2.

The data for cans without electrolyte are shown in Table 2 as well for an easy comparison with the other results obtained.

TABLE 1. IRON CONTENT OF THE ANODE AND THE ELECTROLYTE

Storage Weeks	Lithium Height (inches)	Iron in the Electrolyte (mg)	Iron on Lithium (mg)	Total Iron (mg)
1	0	3.121	-	3.121
	0.5	1.360	0.002	1.362
	1	1.850	0.007	1.857
	1.5	1.490	0.032	1.523
2	0	3.872	-	3.872
	0.5	1.793	0.004	1.797
	1	1.812	0.009	1.821
	1.5	2.575	0.022	2.597
4	0	4.462	-	4.462
	0.5	2.450	0.002	2.452
	1	1.903	0.004	1.906
	1.5	2.050	0.004	2.054

TABLE 2. IRON CONTENT OF THE ELECTROLYTE AFTER STORAGE WITH CANS IN CONTACT WITH CATHODES

Storage (weeks)	Cathode Height (Inches)	Iron Content (mg)
1	0	3.121
	0.5	4.005
	1.0	3.046
	1.5	4.151
2	0	3.872
	0.5	4.783
	1	4.717
	1.5	5.409
4	0	4.462
	0.5	4.462
	1	3.971
	1.5	3.872

2.2 DISCUSSION

It is evident from the results in Table 1 that the anode in contact with the can reduces the amount of iron generated by corrosion by approximately a factor of 2 relative to the amount found in the experiments involving cans alone. It is also evident that most of the iron generated by corrosion remains in the electrolyte even after the longest period of storage of 4 weeks. With the exception of the 4 week group, the iron content of lithium is proportional to the surface area of the lithium foil used. Small differences between the results for various periods of storage suggest a rapid reduction of the corrosion rate with time within the first week of storage and a relatively insignificant increase in the iron content beyond the one week period.

Table 1 also shows two unpredictable results. First is the fact that the iron content found on lithium does not increase beyond the first week of exposure for any of the tests conducted. It almost suggests some sort of self inhibition by iron of the exchange reaction between the metallic lithium and iron species in the solution. A rough estimate of the amount of iron distributed over this lithium surface could be made by considering the total amount of iron detected and the total surface area of lithium involved. The result was of the order of magnitude of $3.77 \cdot 10^{-7}$ g of iron per cm^2 of lithium surface, or the thickness of iron film on lithium of 4.83 Å, assuming no alloying effects between lithium and iron. Since the presence of lithium chloride on the passivated lithium surface has been established (2) one must assume that iron does not form a uniform film on lithium but, rather, must be scattered around and incorporated into voids of the lithium chloride film. The combined effects of these two substances was a total passivation of lithium surface, demonstrated in D size cells with iron added to their electrolyte. (3)

The second fact indicated in Table 1 is an apparent independence of the total iron generated on storage upon the bare surface area of the can. Although the surface areas investigated varied only for a little over a factor of 2, one should expect more iron formed on a larger surface area exposed. There is no explanation for this phenomenon at the moment and the matter, obviously, should be explored in more detail.

The tests with cathodes, Table 2, showed approximately twice the amount of iron generated by corrosion, relative to the results obtained in the tests with anodes. In fact, the amount of iron generated in contact with cathodes is the same as that found in tests with cans alone, suggesting that the contact with the cathode has no effect on the rate of corrosion of stainless steel hardware.

3. REDUCTION OF $SOCl_2$ ON STAINLESS STEEL

3.1 EXPERIMENTAL AND RESULTS

The study of self discharge reactions involving the reduction of $SOCl_2$ on the surface of stainless steel hardware was conducted in the glass cell arrangement described in the preceding report. The working electrode was a round disc of stainless steel having a surface area of 5.69 cm^2 (both sides). The lithium reference electrode was placed directly above the back side of the working electrode in its own compartment separated from the bulk of solution by a fine glass frit. The working electrode compartment and the lithium counter electrode compartment contained 200 ml of electrolyte each and they were also separated by a glass frit. The working electrode was maintained at the reference potential of lithium, while the current was monitored between it and the counter electrode. The measurements were conducted over a period of 125 to 160 hours at each of the three selected temperatures, 25°C, 55°C, and 72°C. The current decay with time is shown in Figures 1, 2, and 3 for the above three respective temperatures. Typical figures measured at particular time intervals are also shown in Table 3 for an easier comparison of the behavior at different temperatures.

3.2 DISCUSSION

The electrochemical reduction of thionyl chloride in the $SOCl_2$ electrolyte results in a formation of LiCl on the cathode surface. Since the electrolyte used is already saturated with LiCl, at a given concentration of $AlCl_3$, the product of the reduction must precipitate on or in the immediate vicinity of the cathode surface, depending on the geometry of the electrode structure. LiCl has been identified by others (4) as a solid product formed on the surface of cell hardware in contact with lithium. We have now generated quantitative data which could be used to make some estimates of the rate of self discharge caused by this reaction.

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TABLE 3. REDUCTION CURRENT DECAY ON STAINLESS STEEL AT VARIOUS TEMPERATURES

Time	Current density, mA/cm^2		
	25°C	55°C	72°C
1 second	0.53	35.15	17.50
10 seconds	0.40	8.79	8.75
60 seconds	0.31	2.60	3.69
2 hours	0.10	0.50	2.09
24 hours	0.05	0.15	0.38
100 hours	0.03	0.07	0.14
120 hours	0.01	0.02	0.12

The initial surges of high self discharge current at each of the three temperatures are of no serious consequence to the loss of capacity, since they occur over a short period of time. Relatively steady current, reached after, say, 120 hours, could be used to make necessary estimates of the maximum losses of capacity on storage. Assuming a total bare interior surface of D size can be 58.65 cm^2 (as in the wound cell) and the discharge currents of 0.12, 0.02 and 0.01 mA/cm^2 for the three respective temperatures, one could estimate what the self discharge rates would have been if the experiments in the glass cell were a valid representation of the conditions prevailing within the sealed cell. For the 13 Ah cell capacity losses would amount to:

3.21 percent per month at 25°C
6.42 percent per month at 55°C
38.93 percent per month at 72°C

These estimates should be compared with the results obtained in the course of studies of voltage delay phenomena, described below.

4. VOLTAGE DELAY OF CELLS MADE WITH STAINLESS STEEL CANS

Storage tests were conducted with the wound D cells, made according to computer aided design and built with stainless steel cans as the anode terminals of the cell. The particulars of that design as well as the actual dimensions of the components of the electrode structure have been described in the preceding report. Six cells, hermetically sealed, have been stored for one month, two each at each of the three temperatures. The voltage delay was tested at a moderate discharge rate of 1 mA/cm^2 only and defined as anytime the cell voltage remained below 2V at the beginning of discharge. A complete discharge followed the voltage delay test and the data obtained are presented in Table 4, with the individual discharge curves shown in Figures 4 to 9.

The capacity losses at 55°C and 72°C were calculated relative to the capacity obtained with the cells stored at room temperature for the one month. A comparison of these loss rates with those predicted from the experiments with the glass cell shows a reasonably good agreement considering radical differences in the geometries of the electrode structures and in the ratios of active surface areas to the volumes of the electrolyte involved. Had the experiments in the glass cell been continued for the same period as the storage of the cells, the average monthly losses, due to the current decay with time would probably converge.

It is obvious from the earlier experiments with cold rolled steel cans that stainless steel cans must be used. It is also obvious from these experiments that the stainless steel cans should not be attached to the anode terminal, if the cells are required to withstand prolonged storage at elevated temperatues. A logical solution to these problems is achieved with the reversal of the cell polarity, i.e., compromising between an increased rate of hardware corrosion and an increased rate of self discharge, unless some other hardware material could be found that would not be subject to corrosion in contact with the cathode material.

TABLE 4. VOLTAGE DELAY AND CELL CAPACITY OBTAINED AFTER STORAGE OF ONE MONTH AT VARIOUS TEMPERATURES

Temp. °C	Cell No.	Voltage Delay (Seconds)	Capacity (Ah)	Loss %/Month
25	1	0	13.4	0
	2	0	13.2	
55	3	210	12.8	3.7
	4	3	12.8	
72	5	0	9.5	28.5
	6	0	9.6	

5. CORROSION TESTS WITH KOVAR

Preliminary tests were carried out with Kovar as a possible hardware material. Kovar was tested in three different situations, relative to the active electrode materials:

- with a piece of lithium attached
- with a piece of carbon electrode attached
- with no attachments of electrode materials

The sample was weighed before and after the test to see if a loss of weight during the test could be detected directly. The tests consisted of a continuous boiling (refluxing) of the sample material in the electrolyte for eight days and a subsequent analysis of the electrolyte for Ni, Co and Fe. The electrolyte analysis was done at the beginning of the experiments as well, in order to establish starting contents, if any, of the three major constituents of Kovar. The volume of the electrolyte used in each of the tests was 200 ml. The results obtained are shown in Table 5.

Lithium foil used in the tests was analyzed separately by a method described earlier and was found to contain only a fraction of ppm of each of the three elements. This, combined with the fact that the amount of lithium involved was several times smaller then the amount of Kovar, makes this portion of the content of three elements negligible.

Preliminary experiments clearly suggest the use of Kovar as a possible alternative to stainless steel as a hardware material for the can when it is connected to either the cathode or the anode end of the cell.

TABLE 5. RESULTS OF CORROSION TESTS WITH KOVAR

Test Type	Sample Weight (g)		Electrolyte Content (ppm)		
	Before	After	Ni	Co	Fe
Kovar Alone	3.5607	3.5602	6	5	9
Kovar and Lithium	3.2697	3.2699	5	0.7	2.9
Kovar and Anode	3.5666	3.5661	6	5	9
Electrolyte before test			7	5	9

6. NEXT QUARTER PROGRAM

We are going to continue the study of hardware materials suitable for building $SOCl_2$ cells and batteries. Building cells of stainless steel with an inversed polarity, i.e., with the cathode attached to the can, seems to be the first order of business for the next quarter.

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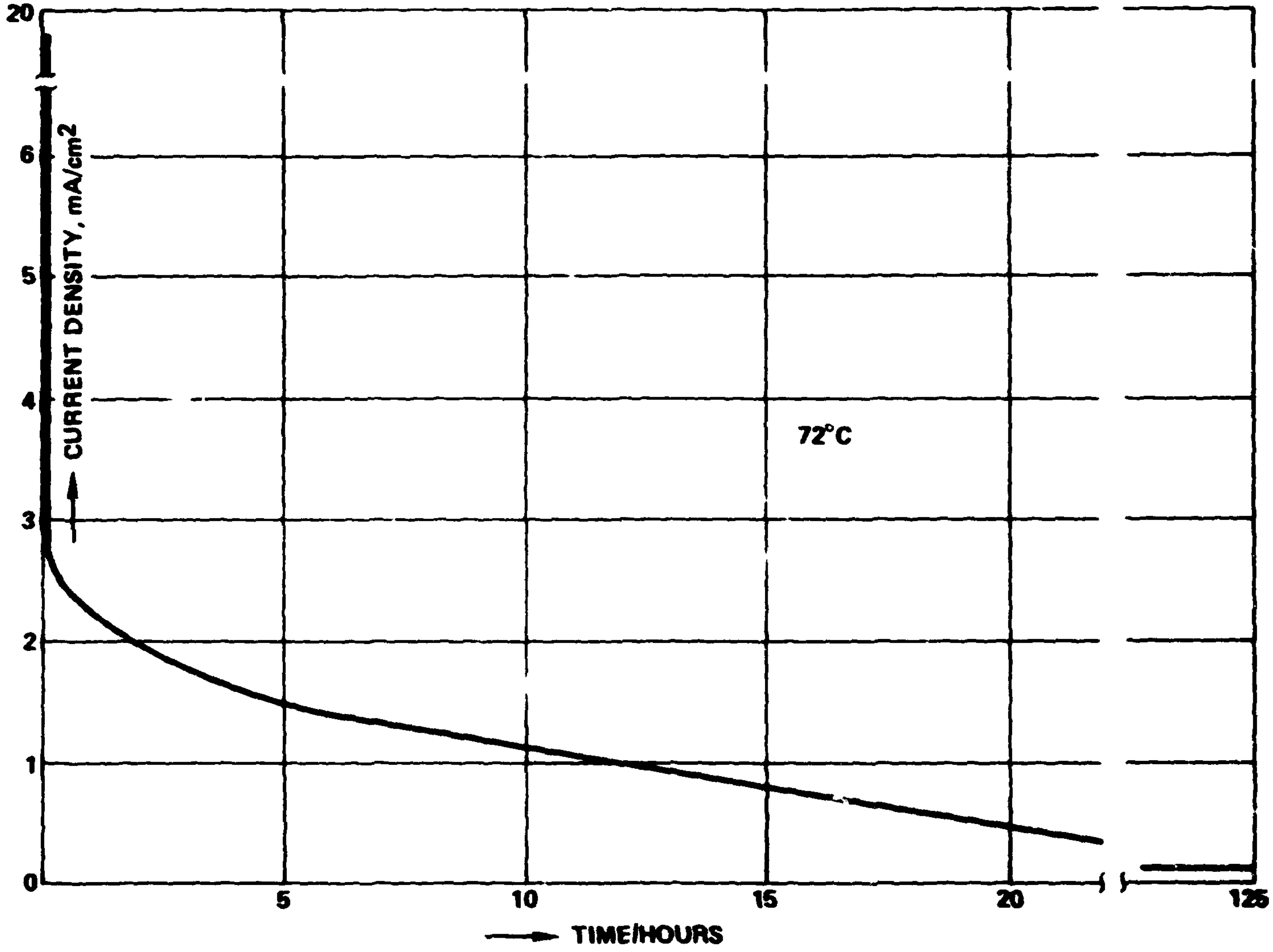
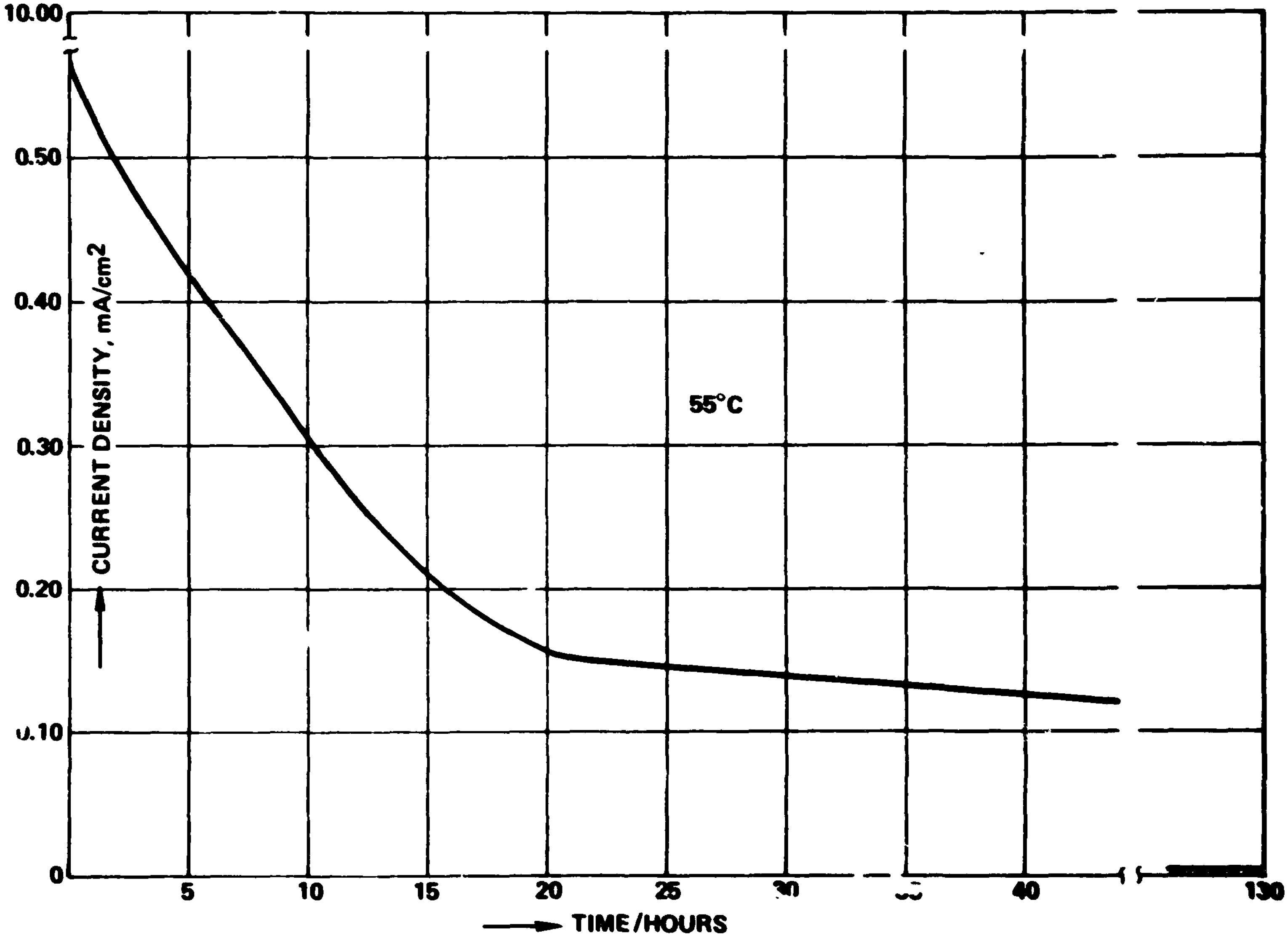


Electrochemical Reduction of Thionyl Chloride on Stainless Steel at 72°C



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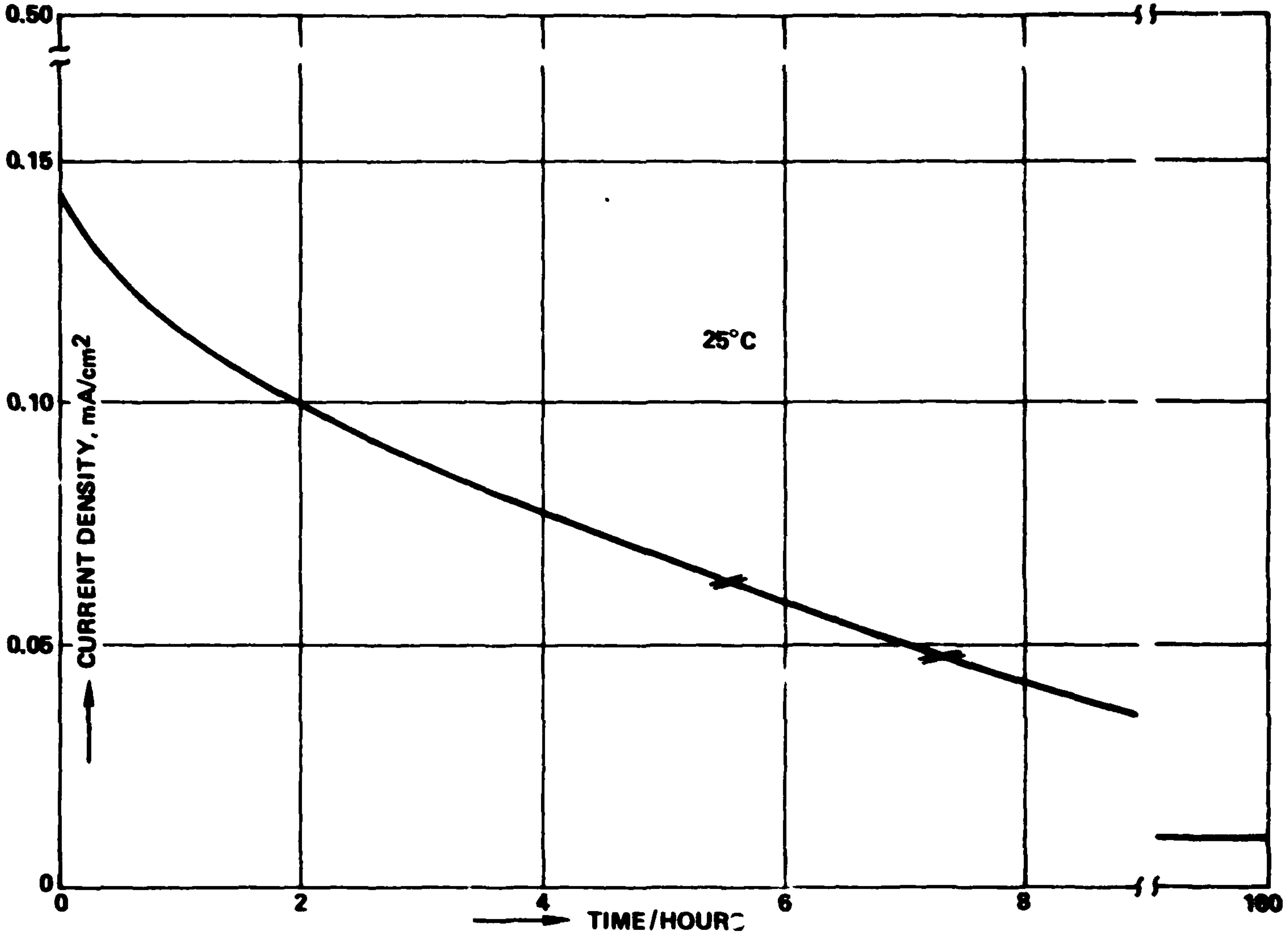

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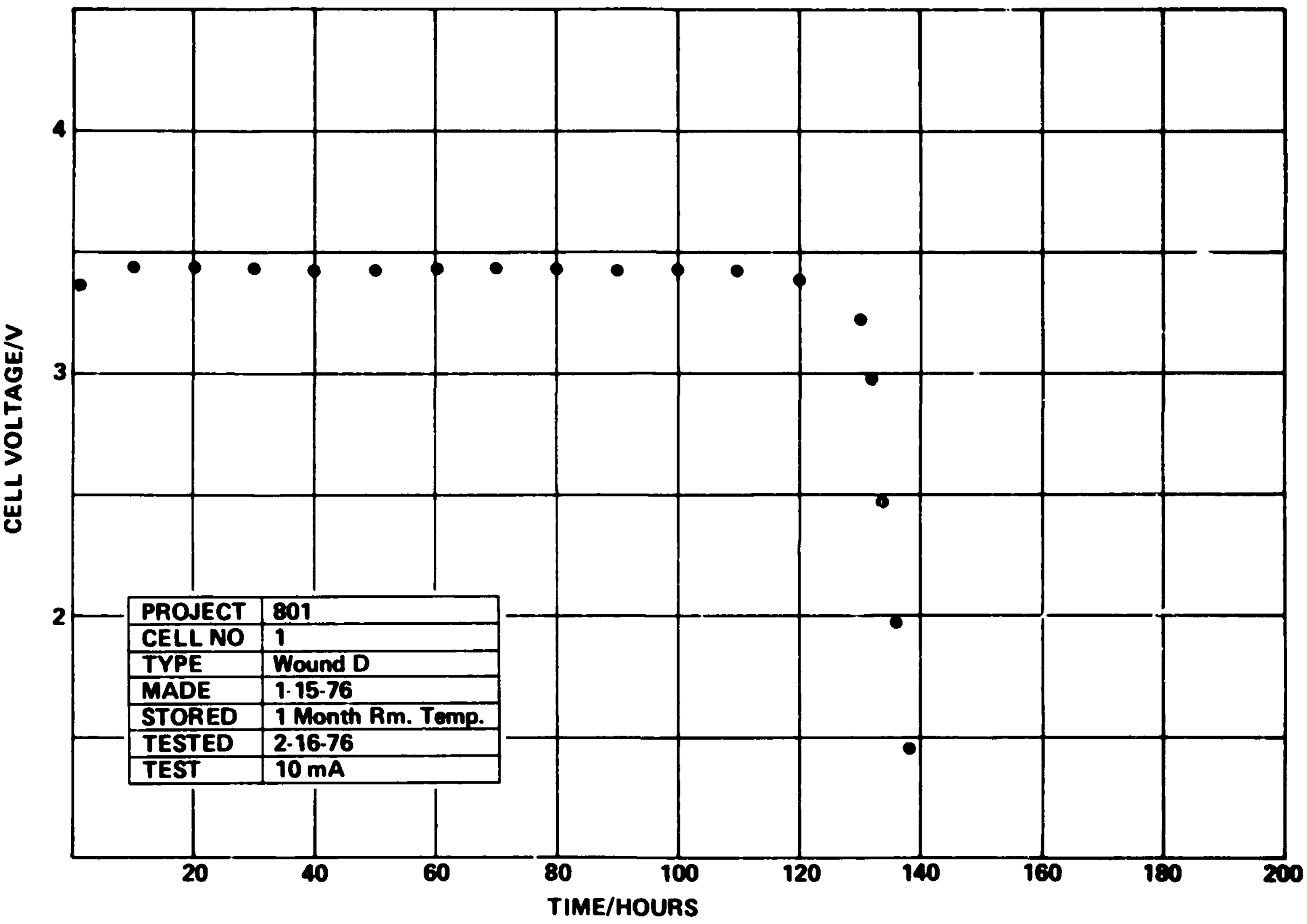

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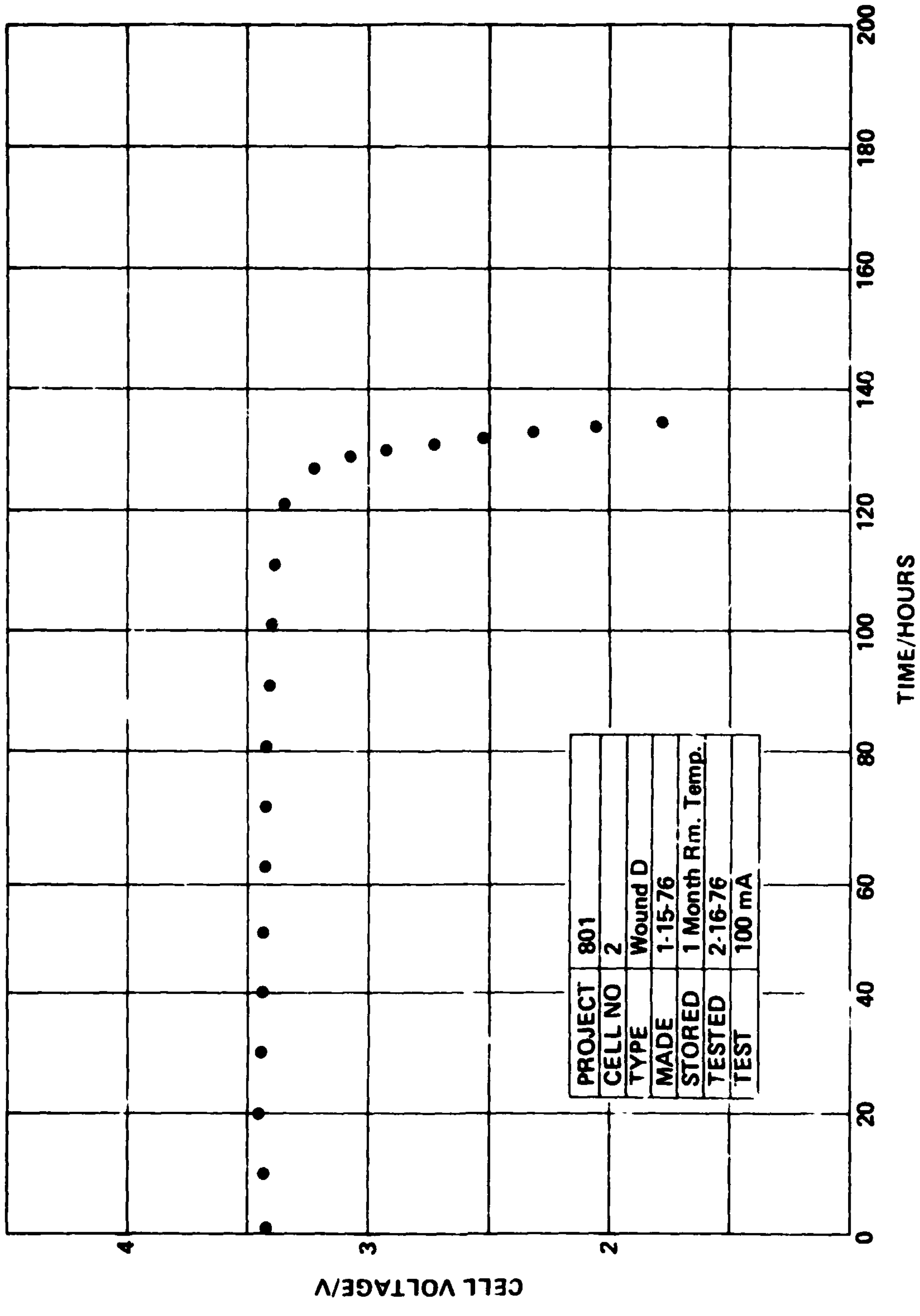
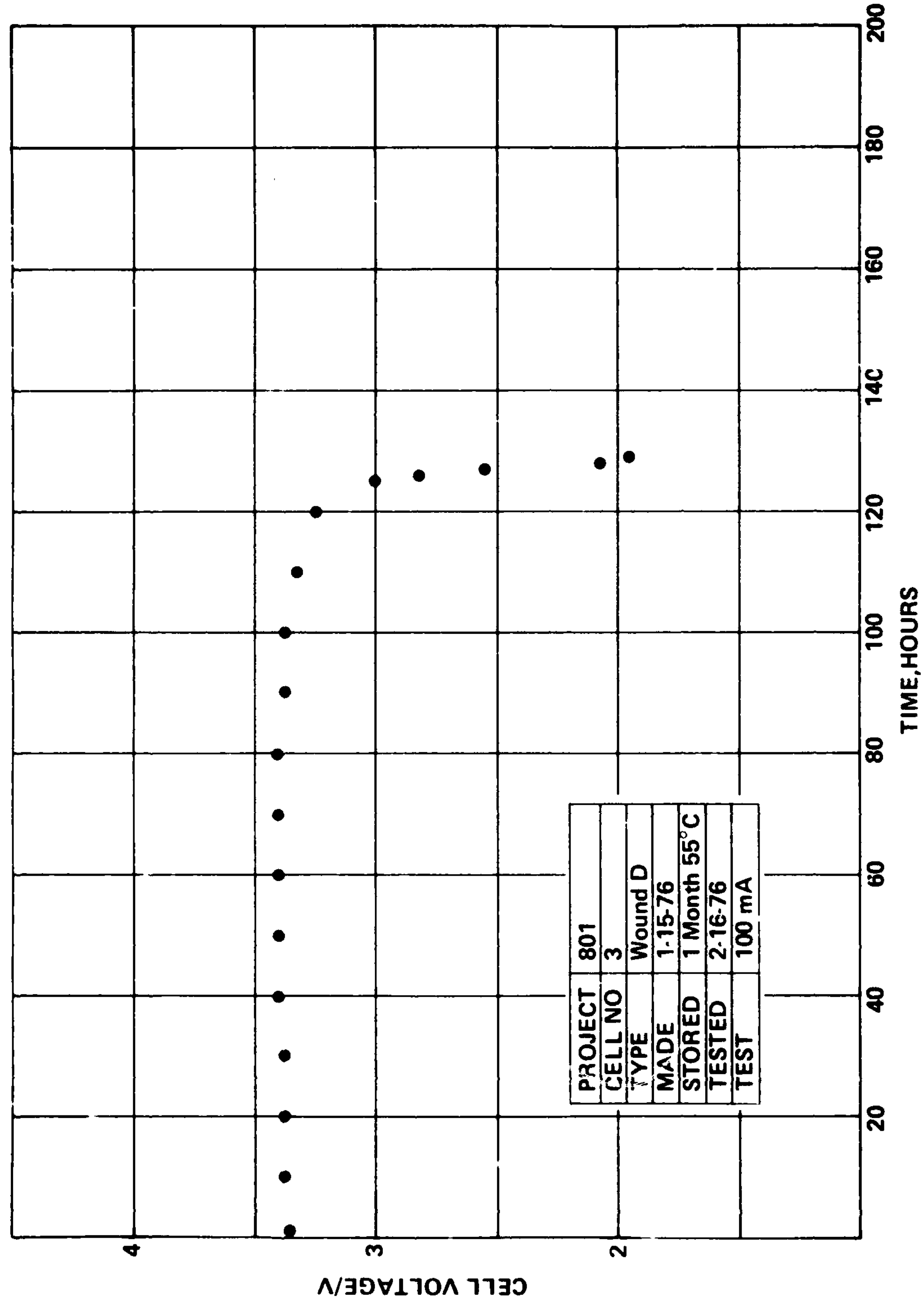
STORED	1 Month Rm. Temp.
TESTED	2-16-76
TEST	10 mA


CELL VOLTAGE/V
4
3
2
TIME/HOURS
0
20
40
60
80
100
120
140
160
180
200
PROJECT 801
CELL NO 2
TYPE Wound D
MADE 1-15-76
STORED 1 Month Rm. Temp.
TESTED 2-16-76
TEST 100 mA



CELL VOLTAGE/V
4
3
2
TIME,HOURS
20
40
60
80
100
120
140
160
180
200
PROJECT 801
CELL NO 3
TYPE Wound D
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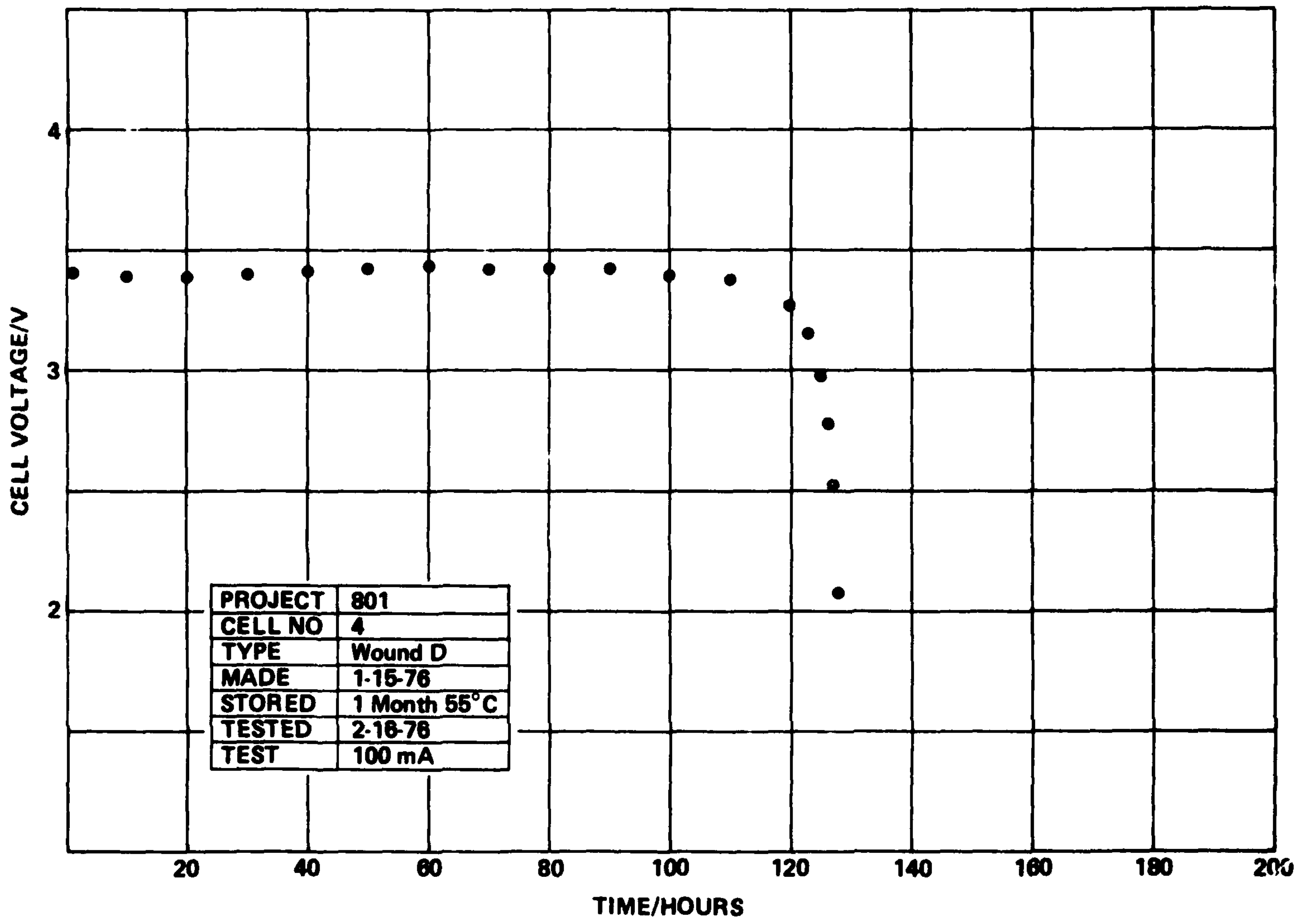
STORED 1 Month 55°C
TESTED 2-16-76
TEST 100 mA



CELL VOLTAGE/V
4
3
2
TIME/HOURS
20
40
60
80
100
120
140
160
180
200
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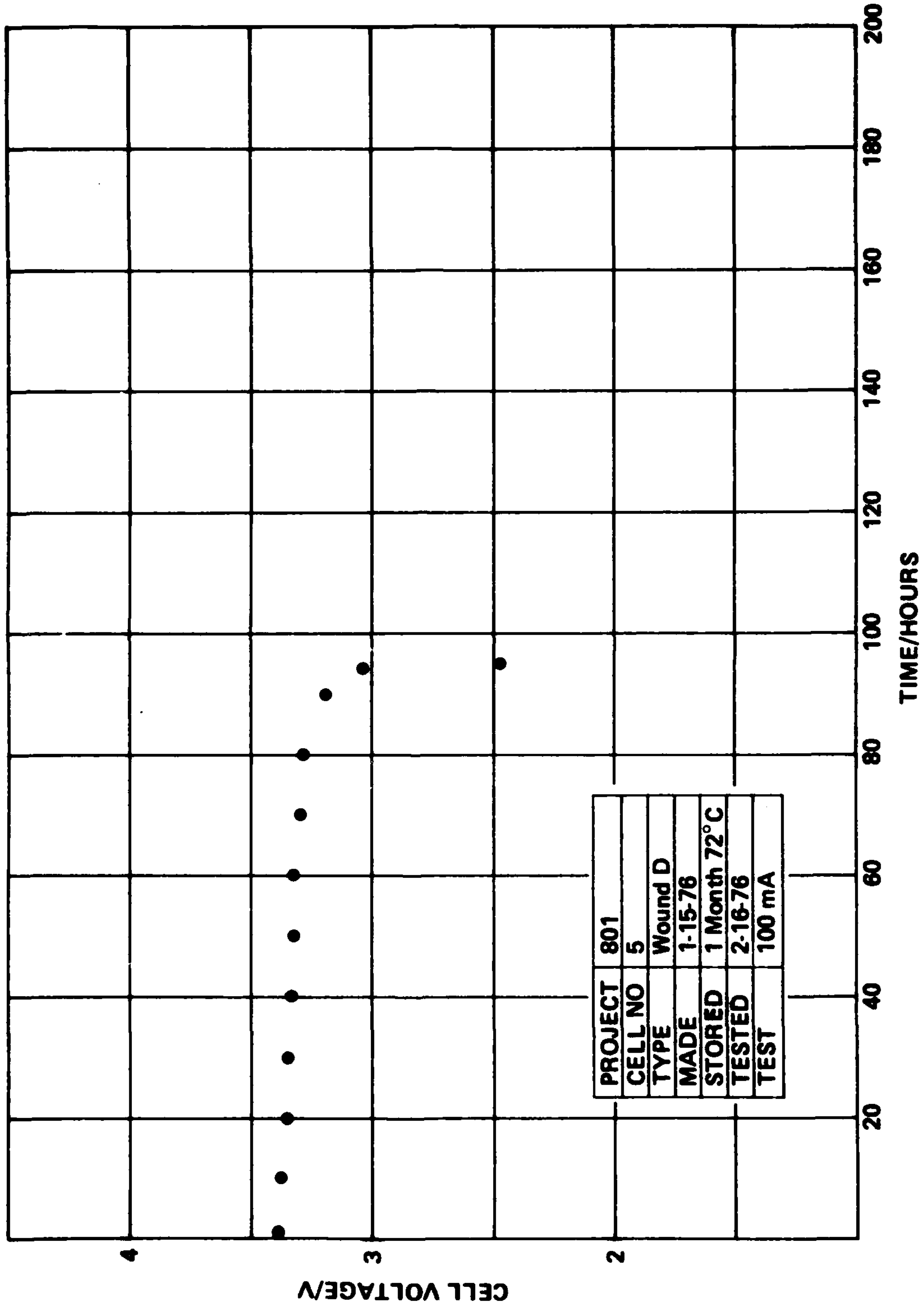

CELL VOLTAGE/V
4
3
2
TIME/HOURS
20
40
60
80
100
120
140
160
180
200
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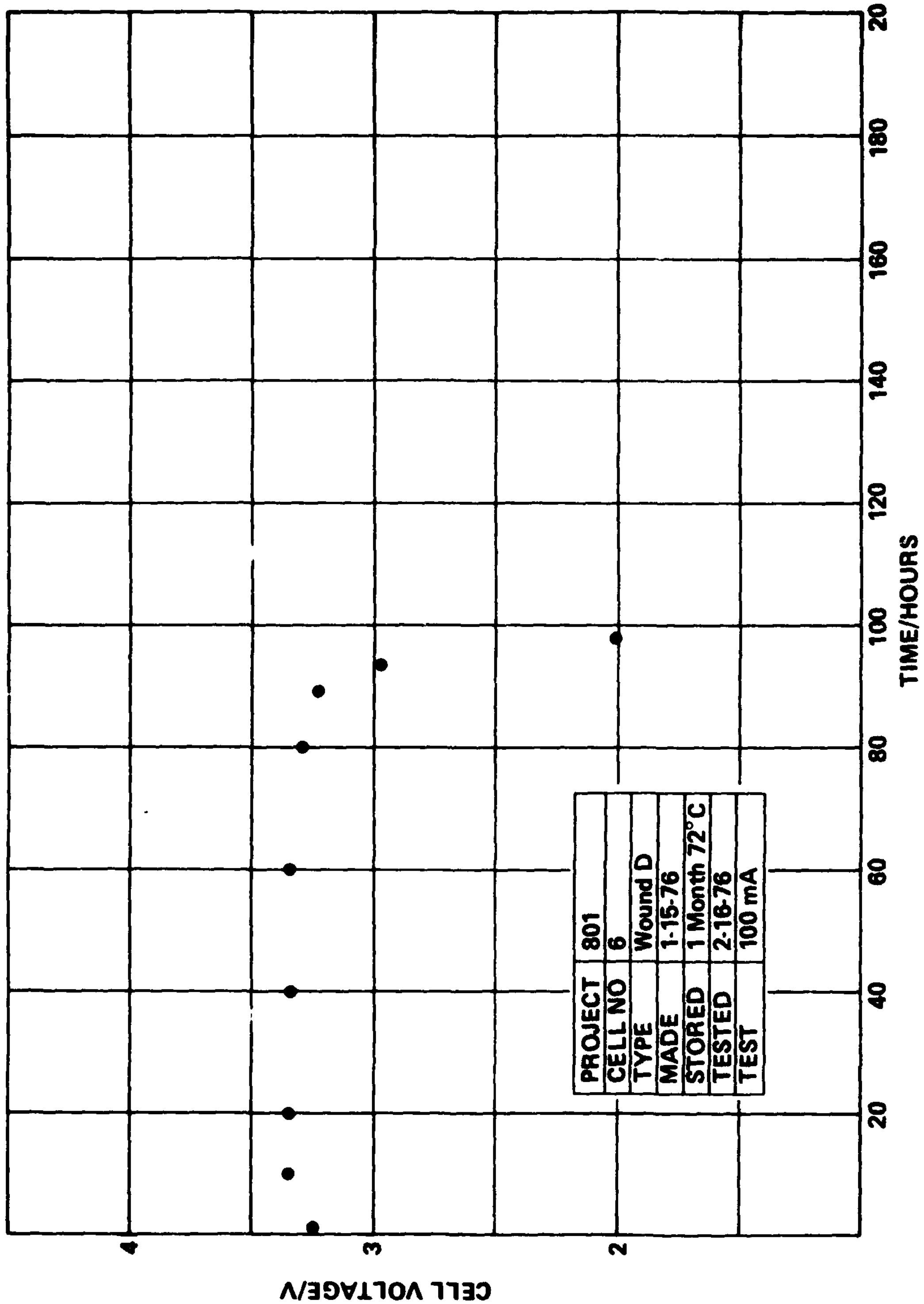
TEST 100 mA


CELL VOLTAGE/V
4
3
2
TIME/HOURS
20
40
60
80
100
120
140
160
180
20
PROJECT 801
CELL NO 6
TYPE Wound D
MADE 1-15-76
STORED 1 Month 72°C
TESTED 2-16-76
TEST 100 mA