

LITHIUM BATTERY DISCHARGE TESTS

C. Johnson
Boeing

I would like to report today on the preliminary results of the lithium cell discharge tests that we have been conducting at the Boeing Company for about the past year.

These results are preliminary in that the test is ongoing and it will continue for several years into the future. But, they are indicating some interesting things, and we wanted to present the data that is presently available.

The test is different from most discharge tests in that it is extremely low rate. What we are looking for is long-term applications for lithium cells.

(Figure 2-53)

The objective of the test is to characterize the long-term discharge of a vast variety of lithium cells that are currently available and to test the susceptibility that cells have to chemical variation during the very slow discharge.

We know the lithium electrode is extremely active, and chemical reactions will tend to parasitize or to rob the lithium from the reaction we would like to produce, the electrochemical generation of energy. The technical approach that we are taking is to detect this chemical degradation by using the extremely long-term testing.

What we are doing is measuring the voltage as a function of time; what we are looking for are to see preliminary failures that occur as evidenced by the drop in voltage prematurely to the expected cell life.

Basically what we are doing is to set a very small shunt resistor, or a very large shunt resistor, across the cell terminals and to monitor the voltage as a period of time. We calculate the resistance value such that the cell will be drained in the specific time period. The times that we are testing are 1/4, 1/2, 1 year, 2 years, 4 years, 8 years, and even 16 years of discharge.

Now, of course, the question that immediately comes to mind is, who wants to wait around for 16 years for the test results? Our answer to that is that we don't plan to wait 16 years. We are hoping to find those systems that will be able to withstand the chemical degradation, to maintain their voltage during that time, and to eliminate those systems that show problem areas during the voltage discharge.

The hypothesis that is being tested is that the lithium electrode is very active. One reason that it does not chemically react is that it forms a passivating layer on the lithium surface.

What we are doing during the low-discharge rate is maintaining an active lithium electrode. We are assuming that the chemical degradation reactions will be more prevalent during this active time of the electrode.

So, what I would like to show next is the vast number of systems that we have in test at this time.

(Figure 2-54)

As you can see, there are more systems than these available now. But these are the systems that we have tested: the lithium carbon monofluoride, lithium copper oxide, lithium iodide, lithium iron, sulfide, the lead iodide system and manganese dioxide, and the silver chromate. Two that have been reported on quite a bit today are the lithium sulfur dioxide and the thionyl chloride system. We also had some cells from the vanadium pentoxide.

I have listed the chemical designations and used several abbreviations as I have enumerated at the bottom of this figure.

(Figure 2-55)

The kind of results that we are getting is a lithium carbon monofluoride system that has been discharged at a rate of a force of a year. As you can see, the voltage maintains its value to the calculated cell life. This cell, we would expect, has met the criteria of the test and does not show appreciable chemical degradation during slow rate discharge.

(Figure 2-56)

The lithium copper oxide system at a 1-year rate has shown some premature failure, although it is not very severe. The cell voltage did drop off before the calculated cell life was attained.

(Figure 2-57)

Another cell which was being discharged at a 2-year rate has already failed at less than 40 weeks, and the cell voltage fluctuated slightly, showing these voltage fluctuations and then premature failure as the voltage dropped off at a time much less than the calculated cell life.

(Figure 2-58)

Another system, the lithium iron sulfide system, shows to be very promising.

(Figure 2-59)

During the 1/2-year rate shown here, two cells essentially met the calculated cell life, and another cell which was discharged at another rate also met the calculated cell life. Perhaps the longer timeframe will show up some additional results. But this is what we have at this point.

(Figure 2-60)

The manganese dioxide system looks to be fairly favorable at a 1/4-year rate. The cell has discharged a little bit prematurely, but has essentially met the requirement.

(Figure 2-61)

As we increase the time or decrease the rate at which we are discharging, we find that one of two cells in this slide has experienced some premature failure, and the voltage has dropped off prematurely. The other cell seems to have met the requirement.

(Figure 2-62)

We have another cell which we are discharging at a 1-year rate, and it is also showing premature failure in dropping off in cell voltage.

(Figure 2-63)

This is the lithium sulfur dioxide system that we have tested. These are actually three cells plotted on the same chart. You can see two of the cells have lost their voltage prematurely, whereas one of the cells came very close to meeting the expected or calculated cell life. These were discharged at a 1/2-year rate.

(Figure 2-64)

Similar cells discharged at a 1-year rate show much the same phenomena with all the cells discharging prematurely.

(Figure 2-65)

We have two cells being discharged at a 2-year rate, and already one of the two cells has experienced premature failure. The other cell is continuing in voltage. We are looking to see when it might lose its voltage also.

VOICE: Are these at room temperature?

JOHNSON: Yes, they are at room temperature.

(Figure 2-66)

The lithium thionyl chloride system is being discharged at a 1/2-year rate; two cells are showing discharge prior to the calculated cell life, but very close to meeting the expected cell life.

(Figure 2-67)

At our 1-year rate, we see that the voltage dropped off a little bit more prematurely than the previous figure showed. We have to wait to see what the 2-and 4-year rates will show on this system.

(Figure 2-68)

The lithium vanadium pentoxide system shows a characteristic two-step voltage discharge, discharging first at about 3.3 volts and then dropping down to second plateau. This second plateau would be expected to reach the calculated cell life, although we experience a premature failure and the voltage drops off prematurely.

Well, it is still early in the test to come to any definite conclusions. But, the results are indicating that several of the lithium cell systems may be susceptible to chemical degradation over a long period of time. And this, of course, decreases the expected cell life.

The conclusion that can be made is that the test does show some promise as a useful criterion of measuring those systems which are susceptible to chemical degradation. Or perhaps, more importantly, it would be those systems that are not susceptible to the chemical degradation.

The future work we have planned is that during 1980, we plan to add additional systems to the tests and to fill out the test matrix to include three specimens ourselves for each discharge timeframe.

Also, we would like to add some control specimens which we plan to leave at open circuit voltage to monitor their voltage during the same time period.

DISCUSSION

BIS: Are these all research cells, or are these commercially available cells?

JOHNSON: These are essentially commercially available cells that we have in test, yes.

BIS: Could you identify some of the more prominent ones like thionyl chloride and the SO₂? Who the manufacturers were?

JOHNSON: At this point, we have cells from most of the major manufacturers. I don't think it is fair to specifically identify specific manufacturers because, first of all, the test is an ongoing

st, and the results are preliminary at this stage. We are not in the business to critique manufacturers.

BENNETT: Can you tell me whether or not all these cells are being discharged in the same orientation, and what orientation is that?

JOHNSON: I would say that the cells are being discharged in a vertical orientation. Does that answer your question?

BENNETT: The header part of the cell was in the upright position then?

JOHNSON: Most of them are C cells or D cells, and they are laying . . .

BENNETT: On their side?

JOHNSON: Yes.

THORNELL: Do you do any storage weight measurements on these long discharges?

JOHNSON: No, we haven't done any weight measurements during discharge.

MALACHESKY: You made a point that you are looking at chemical degradation. Is it possible some of these premature failures that you see are, in fact, due to the failure with the krebs meals that are on these calls? Have you looked for a visible salt encrustation? For example, in the manganese dioxide cells?

JOHNSON: We do examine the cells after they are discharged, and we have not seen any specific problems on that particular system or other systems.

VASANTH: I would like to know whether chemical analyses are done after the discharges are connected? And whether you find any difference from one to the other?

Of course, there should be a difference because you have been studying a various number of cells. Can you throw some light on this aspect?

JOHNSON: We have not dissected any cells at this point. We plan to do some of that in the future. We are planning an expanded test in 1980, and during that test, we do plan to examine cells as they discharge.

VASANTH: At this point, can you say what practices are responsible for the degradation of these cells? Any idea?

JOHNSON: I think there is a variety of systems being tested, and in each one of the systems the degradation process could be slightly different.

Our hypothesis is that we are looking mostly at the lithium electrodes side of the system. But, there have been many indications today that the cathode side of the system is also important. So we are still open on that point.

FELDHAKKE: The data you presented, is that typical data, or is that actually the number of cells that you have under test, two or three in the various types?

JOHNSON: Yes. We have, in many cases, one, two, or three cells being tested of a specific type. When there are several manufacturers of the same cell, then we have additional cells. But, the slides that I showed today were of a specific type.

FELDHAKKE: So you may have tested only two or three cells in some cases.

JOHNSON: Yes, that is correct.

We plan to expand that in this next test and make sure that we have three in each case, plus an additional control test. So there would be four.

TAYLOR: I am going to take this point up again. Did I understand you correctly to say that the results you are getting are representative of all manufacturers for these different systems?

JOHNSON: I may have used the word "slightly" there.

TAYLOR: You have given a series of systems there. And let's face it, SO₂ is one of them. I think that you said also the SO₂s that you were talking about double A-size cells, for example?

JOHNSON: Yes.

TAYLOR: Are you telling me that that is representative of the SO₂ cells made by a group of manufacturers? All of the SO₂ system manufacturers?

JOHNSON: I didn't mean to indicate that, no. We feel that these are preliminary results, and we are going to add to the tests in 1980 to include a lot more manufacturers and more systems. At this point several of the systems involved only one vendor, or maybe two or three.

TAYLOR: I am happy to hear you say that for obvious reasons. I really do think that the conditions you have are, in fact, very benign, room temperature discharge. I am absolutely amazed to see the falloff in performance — you got two out of those three cells.

I do know and have published data, for example, on hermetic cells, which have undergone a charge-up of 1.2-year rate continuous attempts, up to +60°C, without any failures.

Standing that against room temperature over 6 months?

JOHNSON: Some of the data is 1 year. But, yes, we were surprised to see some of the discharges that did occur.

TAYLOR: The point I am making is that I don't think it is really realistic to draw conclusions on that data yet.

JOHNSON: The conclusion I was trying to draw is that the test is worthwhile and we should continue it.

METHLIE: Mr. Johnson, I would suggest that perhaps in each case you could go back to the designer of the cell and ask him for the conditions you were looking at, what the minimum-maximum-medium performance might look at and see how you would rate the groups within that.

LITHIUM-CELL DISCHARGE TEST

OBJECTIVES

- TEST LONG-TERM DISCHARGE CHARACTERISTICS
- EVALUATE VULNERABILITY TO CHEMICAL DEGRADATION

TECHNICAL APPROACH

- DETECT CHEMICAL DEGRADATION BY LONG-TERM TESTING
- EXAMINE VOLTAGE VS. TIME BEHAVIOR DURING DISCHARGE
- INVESTIGATE PREMATURE FAILURES

Figure 2-53

TABLE 1
LITHIUM CELLS IN TEST

LITHIUM/CARBON MONOFLUORIDE	Li/LiBF ₄ , BL, DME, PC/(CF) _n
LITHIUM/COPPER OXIDE	Li/LiClO ₄ , SOLVENT/CuO
LITHIUM/IODINE	Li/LiI/I ₂ -P2VP
LITHIUM/IRON SULFIDE	Li/FeS
LITHIUM/LEAD IODIDE	Li/LiI(AI ₂ O ₃)/PbI ₂ , PbS
LITHIUM/MANGANESE DIOXIDE	Li/LiClO ₄ &LiBF ₄ , DME&PC/MnO ₂
LITHIUM/SILVER CHROMATE	Li/LiClO ₄ , PC/Ag ₂ CrO ₄
LITHIUM/SULFUR DIOXIDE	Li/LiBr, AN&PC/SO ₂ at Carbon
LITHIUM/THIONYL CHLORIDE	Li/LiAlCl ₄ , SOCl ₂ /SOCl ₂ at Carbon
LITHIUM/VANADIUM PENTOXIDE	Li/LiAsF ₆ &LiBF ₄ , MF/V ₂ O ₅ at Carbon

AN = Acetonitrile
 BL = γ -Butyrolactone
 DME = Di-Methoxyethane
 MF = Methyl Formate
 PC = Propylene Carbonate
 P2VP = Poly(2-Vinylpyridine)

Figure 2-54

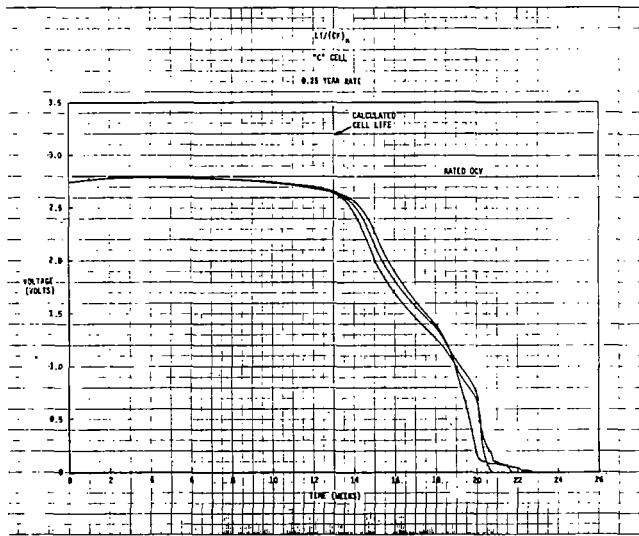


Figure 2-55

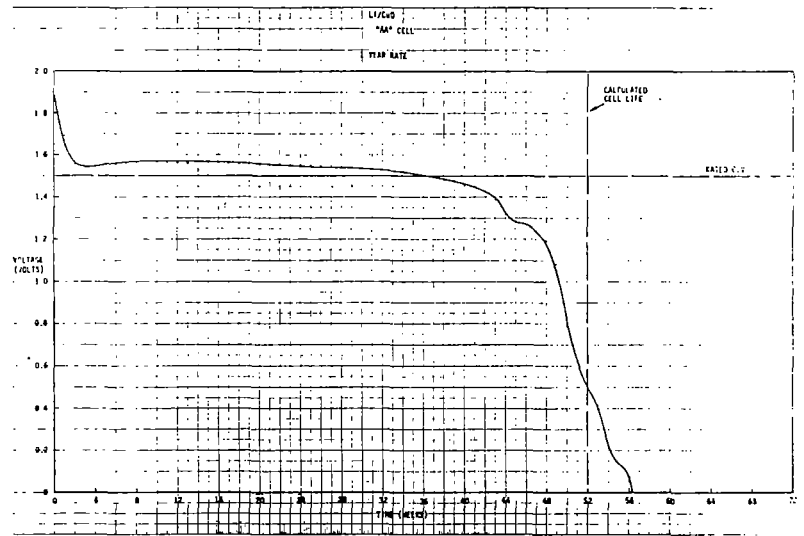


Figure 2-56

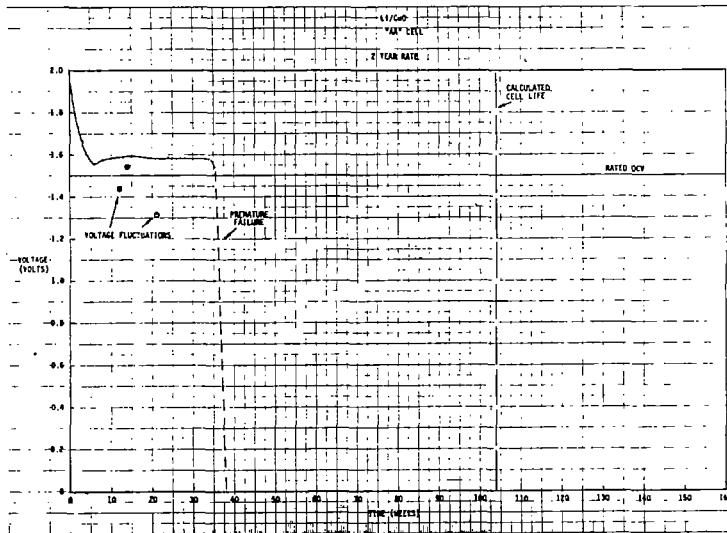


Figure 2-57

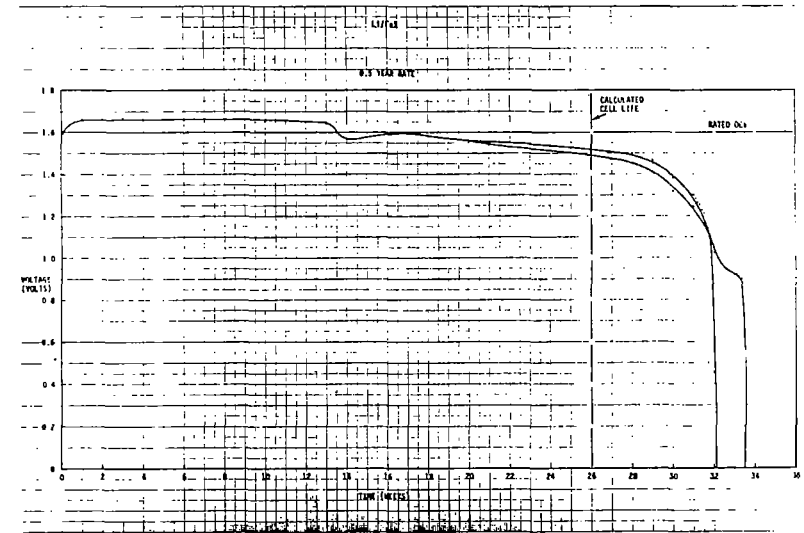


Figure 2-58

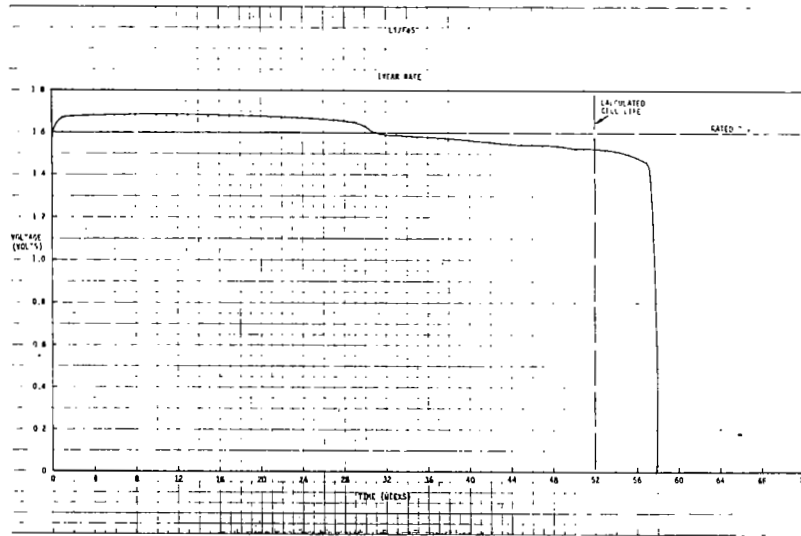


Figure 2-59

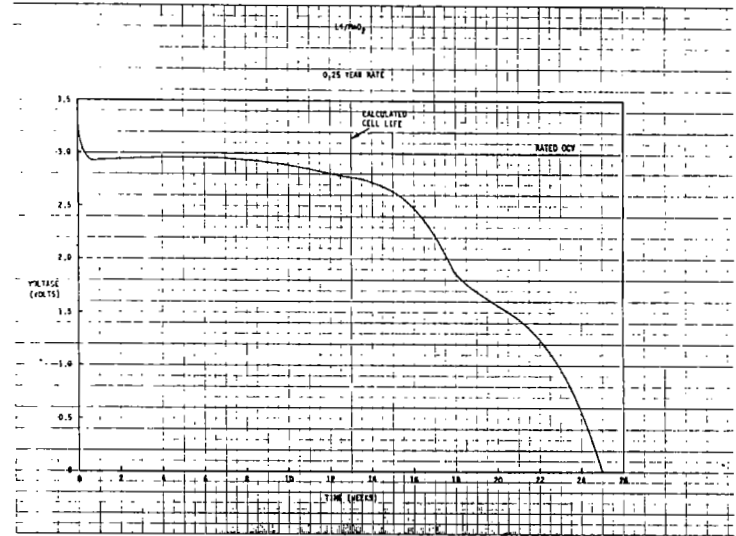


Figure 2-60

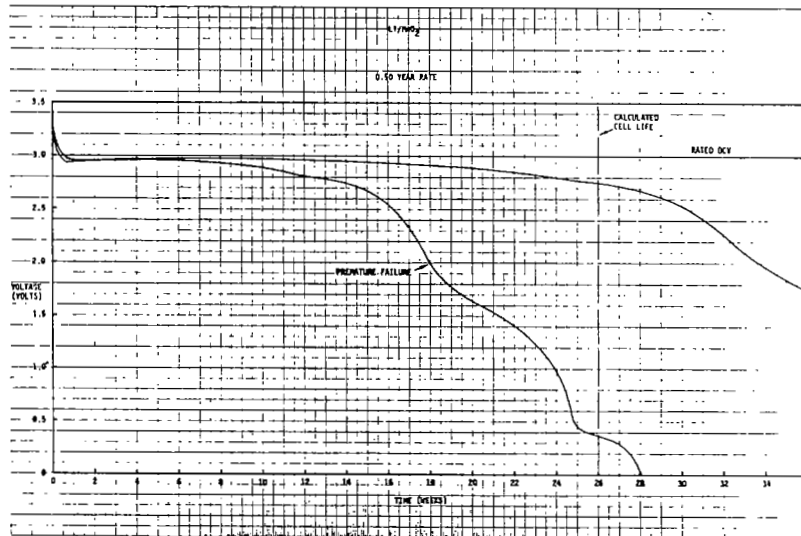


Figure 2-61

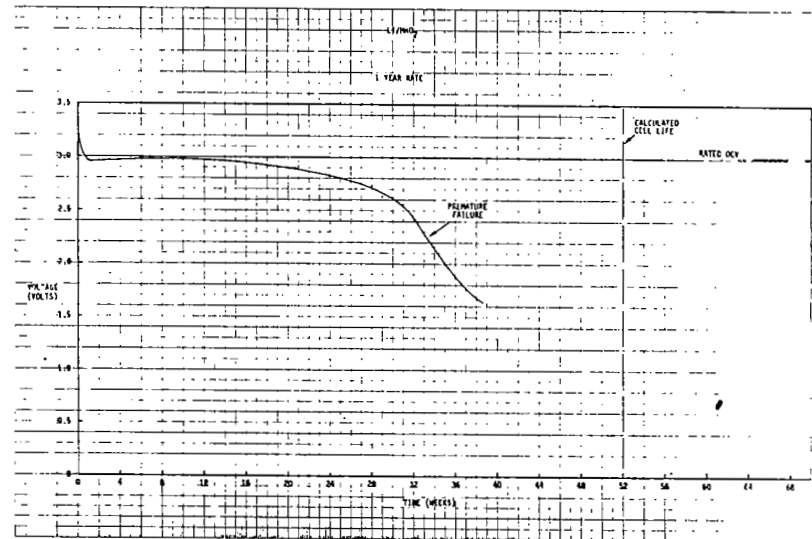


Figure 2-62

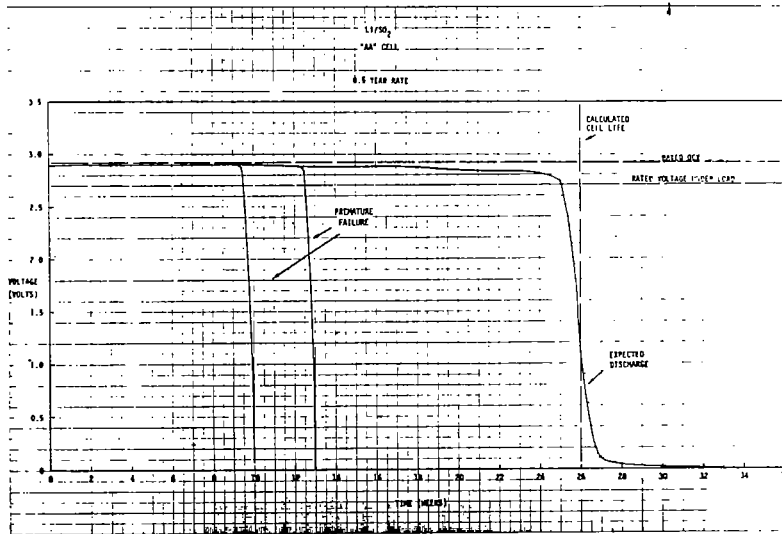


Figure 2-63

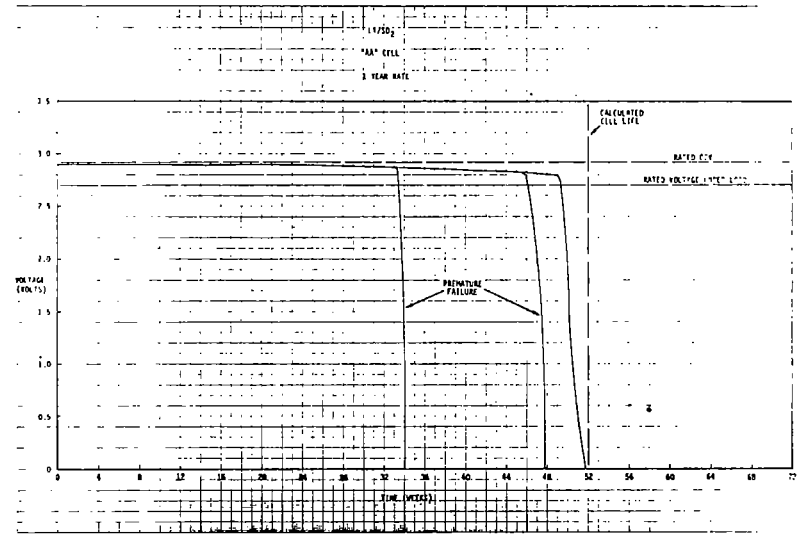


Figure 2-64

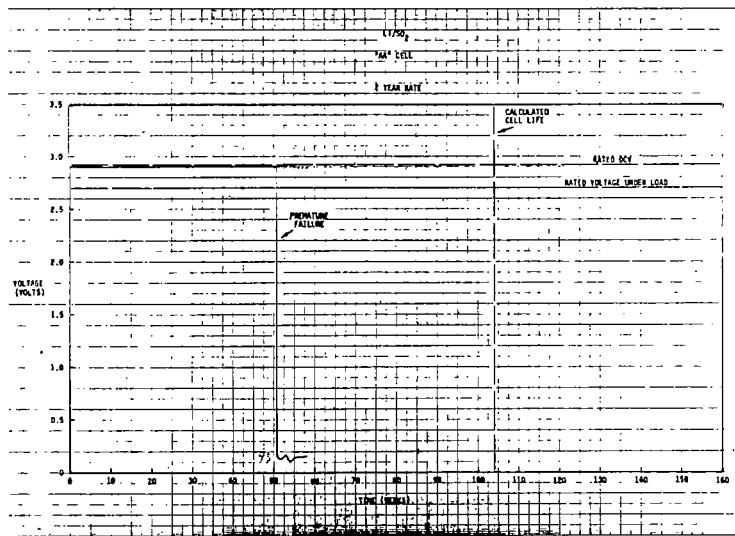


Figure 2-65

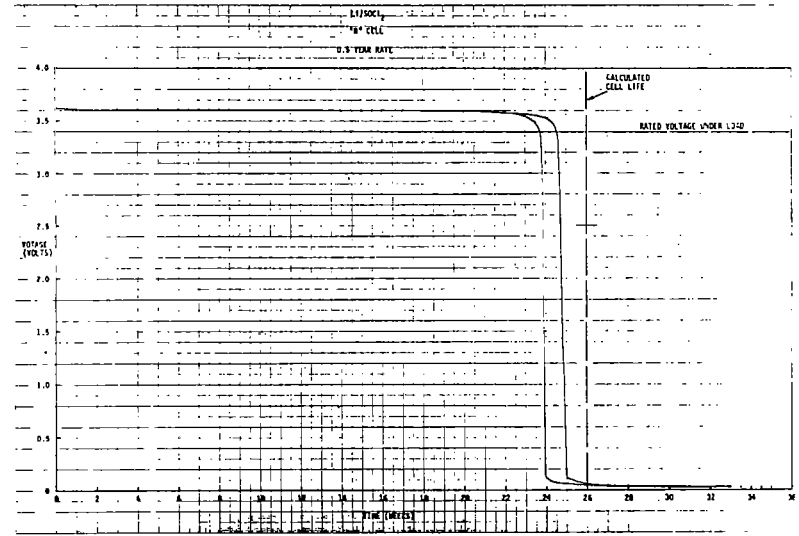


Figure 2-66

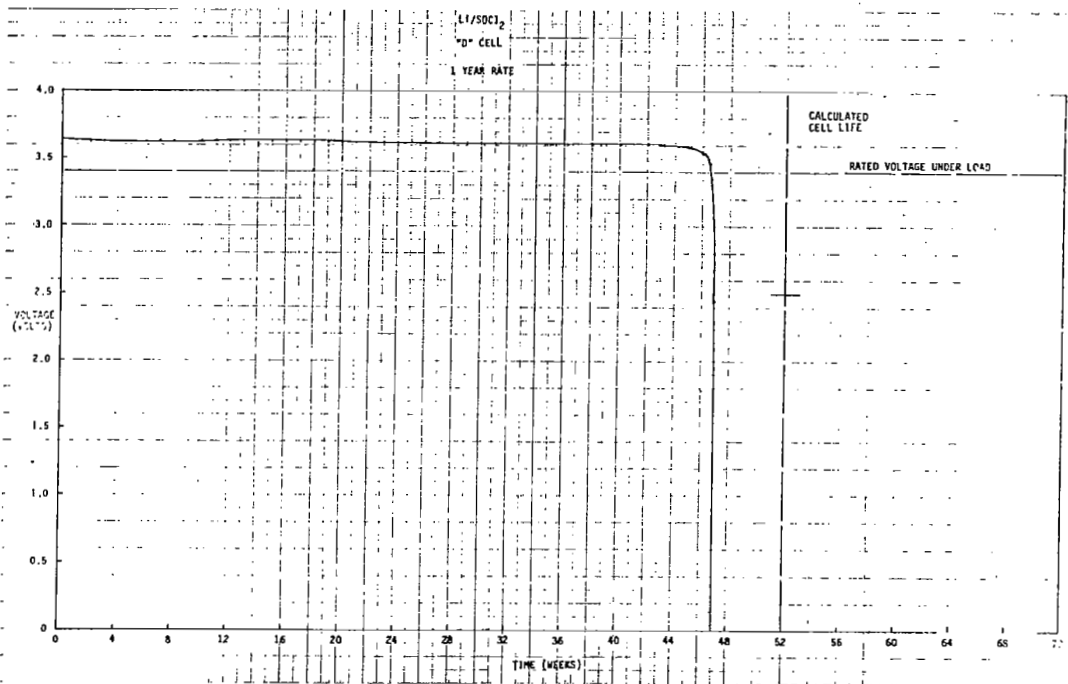


Figure 2-67

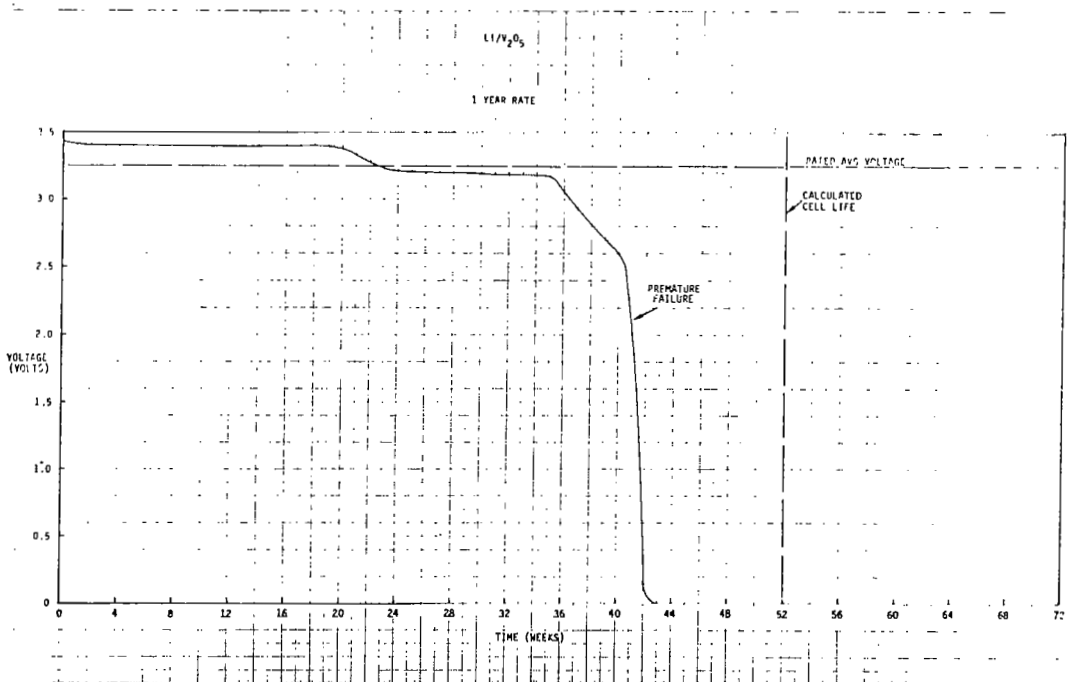


Figure 2-68