

CHARGE CONTROL INVESTIGATION OF RECHARGEABLE LITHIUM CELLS*

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ABSTRACT

An ambient temperature rechargeable Li-TiS₂ cell has been cycled under conditions which simulate aerospace applications. A novel charge/discharge state-of-charge control scheme was used, together with tapered current charging, to overcome deleterious effects associated with end-of-charge and end-of-discharge voltages. The study indicates that Li-TiS₂ cells hold promise for eventual synchronous satellite-type applications. Problem areas associated with performance degradation and reconditioning effects are identified.

INTRODUCTION

Ambient temperature rechargeable lithium cells hold promise as advanced energy sources for future space applications. The Li-TiS₂ couple, with a nonaqueous electrolyte, is the best known ambient temperature system. A battery of this type is of interest due to its expected high energy density (> 100 Wh/Kg) and long life (up to 10 years). However, Li-TiS₂ cell research and technology are in an early development stage with only hand or custom made cells available. In order to further the development of this battery type and assess the state-of-the-art, a cycle life study of a Li-TiS₂ laboratory cell was conducted. The cell was developed at JPL and tested at Rockwell. This paper summarizes the results of this study.

EXPERIMENTAL

Recent cycle life tests conducted at JPL with constant current charge (1 mA/cm²) to 3 volts and discharge (2mA/cm²) to 1.6 volts (100% depth-of-discharge) provided up to 750 cycles with 30% of theoretical capacity remaining at conclusion of the test (see figure 1). The cathode limited cells utilized a LiAsF₆/2MeTHF electrolyte and were of ~ 0.40 mAhr capacity. The tests were voluntarily terminated at the 30% capacity level. Capacity decline, especially during the early stages of cycle life, and cathode deactivation were identified as important problem areas.

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These full charge/discharge results were so encouraging that it seemed appropriate to initiate cycle life tests that would simulate and allow evaluation of the cell for an aerospace application. It was decided to conduct the cycle life testing based on synchronous satellite discharge parameters. Low Earth Orbit (LEO) and many other aerospace applications require a capability of a one-hour or greater discharge rate. The time available for charge is at least 22.8 hours in synchronous orbit operation. It was decided, however, to charge using a taper charge method with a maximum starting current of about the 2.5 hour rate. This should produce a charge time of about four hours allowing the acquisition of four maximum depth-of-discharge (DOD) cycles per day. The taper charge parameters selected would result in full charge cut-off at 2.64 volts with approximately 10 ma charge current flowing. The maximum DOD for synchronous orbit operation is generally in the 50% to 70% range of battery rated capacity in ampere-hours. It was therefore decided to start cycling the cell at 70% DOD until the end-of-discharge (EOD) voltage decayed to approximately 1.7 volts, and then reduce the DOD to 60% until 1.7 volts is reached again, and finally reduce the DOD to 50% and cycle the cell to test termination when 1.6 volts is reached. The EOD voltage was maintained above 1.7 volts during the early cycle testing, because earlier investigation by JPL indicated that accelerated degradation takes place when the Li-TiS₂ cell is discharged to a cut-off of 1.6 volts versus 1.7 volts.

The test parameters described for the cycle test of the cell at synchronous orbit rates and typical maximum DOD are similar to those used in the battery industry for accelerated life cycling of cells/batteries. Similar cycle testing of JPL cells at Rockwell over the past two years provided data indicating that the onset of end-of-life was characterized by a reduction in taper charge current at the 2.64 volt cut-off with successive cycling and a reduction in the elapsed time for charging. The result of reduced charge time and current due to degraded charge acceptance capability was to reduce subsequent discharge capacity and EOD voltage.

It was decided to evaluate a novel charge/discharge state-of-charge (SOC) control scheme designed to overcome some of the deleterious factors leading to the degradation noted above. Where 70% DOD cycling normally takes place between 100% SOC and 30% SOC, the scheme to be evaluated positions the cycling to take place between 90% SOC and 20% SOC, and maintains that position as long as possible. After the cell SOC is established at 20%, the computer controls the SOC by restoring the ampere-hours equivalent to a 70% DOD, and then maintains the SOC range with a charge to discharge (C/D) ratio of one on a coulombic or ampere-hour basis. This approach is made possible by the fact that the Li-TiS₂ couple has a coulombic cycling efficiency close to 100%. This scheme eliminates over-charge and results in a charge completion at a voltage considerably below the 2.64 volt full-charge value. Since both over-charge and excessive charge voltage are factors associated with electrochemical degradation in cell operation, their reduction should contribute to increased cycle life.

In addition, the reconditioning value of charging a degraded cell at a low (30 hour) rate using constant current charge to a voltage cut-off was examined.

CELL AND TEST INSTRUMENTATION DESCRIPTION

The Li-TiS₂ test cell was fabricated at JPL and is an experimental prototype of their own design. The design details are described in table I.

The cycle life tests were conducted in the battery test laboratory at Rockwell, Seal Beach, California. A block diagram of the battery test station with the test cell instrumentation interface is shown in figure 2. The test cell, was contained in a steel pipe safety enclosure, and the enclosure was maintained in an exhaust hood that provided a flow of air over the test cell area to the outside of the building. The temperature of the cell was monitored on its top between the terminals and an additional thermocouple was located on the enclosure baseplate, since the bottom of the cell was in contact with the baseplate for improved heat removal.

RESULTS

Two important variables that result from the application of charge/discharge parameters to control cycle life testing are the end-of-charge voltage (EOCV) and end-of-discharge voltage (EODV). The EOCV with a fixed ampere-hour input reflects the energy level required to store the capacity selected. The ideal response would be a constant EOCV with successive cycles. An increasing EOCV with cycling indicates a capacity degradation process that results in the required voltage increase to store the fixed capacity at a greater energy level. After maximum EOCV is reached, as limited by charge control parameter selection, the capacity stored and available on the subsequent discharge decreases rapidly with further cycling. The EODV indicates the energy level at which the capacity selected for discharge is developed with a given load current. A decreasing EODV is related to degradation processes that increase polarization factors and/or decrease available capacity. Minimum operational EODV is selected based on acceptable system undervoltage and maximum depth-of-discharge degradation effects. For the purposes of this cycle life test, 1.6 volts was selected as the system undervoltage value and 1.7 volts selected as the minimum acceptable cycling voltage. An EODV value below the 1.6 volt system undervoltage limit would signal cell failure and end of the cycle life test. A history of the EOCV and EODV values obtained during the 143 cycles of the cycle life tests are shown in the data plots of figure 3. An Annotation of the Cycle Life Testing shown in figure 3 is provided in table II. The cycle life test can be considered as four consecutive parts. The first part consists of cycles 1 thru 3 where the cell capacity and 20% state-of-charge (SOC) voltage were established.

The results of cycling at 70% DOD are covered by the second part of the life cycle test, cycles 4 thru 84. The first and last cycle

performance at 70% DOD is provided in the charge/discharge data plots, figures 4-7. The effectiveness of a reconditioning method consisting of a low rate, constant current charge was tried during the second part of cycling in cycles 61, 66, 72 and 73. In the cycle 61 charge, the ampere-hour return was limited to the 70% DOD value removed, and therefore accounts for the low EOCV shown in figure 3. The reconditioning charge was not successful as indicated by a lack of improvement in the cycle 61, EODV. In cycle 66 the reconditioning charge was cut off at 2.61 volts and the ampere-hour input allowed to increase correspondingly. Again, the cycle 66 discharge showed a negligible improvement in EODV value. It was decided to try two consecutive reconditioning charges in cycles 72 and 73. Since cycle 72 showed little effect with the charge voltage cut-off at 2.7 volts, it was increased to 2.80 volts in cycle 73. The result was again disappointing and testing of the reconditioning procedure abandoned. The charge to discharge ratio (C/D) in ampere-hours was increased for the first time from one to 1.015 in cycle 75 to compensate for possible degraded efficiency and thereby prevent the EODV from dropping below 1.7 volts. It can be seen in figure 2 that soon after the C/D ratio increase the cell was being charged to the 2.64 volt taper charge limit. At this time the state-of-charge positioning was back to the normal 100% to 30% SOC range.

The results of cycling at 60% DOD are covered by the third part of the cycle life test, cycles 85 thru 105. The improvement in EODV in cycle 80, after a 9 hour open-circuit stand, due to a computer malfunction, led to consideration of an open circuit stand period as a "reconditioning" method. The first open circuit recondition period was tried after cycle 85 discharge. The resulting improvement in cycle 87 EODV was surprisingly good. In cycle 89 thru test completion, a one hour delay after each discharge was included to take advantage of any small reconditioning effect that might be gained.

The results of cycling at 50% DOD are covered by the fourth and last part of the cycle life test, cycles 106 thru 143. The extended open circuit stand period was tried in cycles 129 and 138 as described in table II. The reconditioning effect in cycles 129 and 138 was clearly evident, but of short duration over subsequent cycles. It is theorized that the effect is due to reduction of a temporary polarization condition in the electrolyte and/or TiS_2 plate structure due to relatively high discharge/charge current density operation.

CONCLUSIONS

The results of this cycle life study, together with those carried out at JPL, demonstrate that ambient temperature Li- TiS_2 laboratory cells can be cycled extensively. The potential for eventual use of a secondary lithium battery is very good, especially for synchronous satellite-type applications. There are certainly problems that must be solved, such as capacity decline, and scale-up/systems issues to be addressed. Our understanding of the fundamental processes and degradation modes in rechargeable lithium cells must improve substantially.

Our accelerated cycle life study, using progressive DOD decrease, 70%, 60%, 50%, has provided a good set of baseline data to be used for future test data comparison. The state-of-charge control scheme evaluated shows good promise as a means of extending cycle life, and provides, in the EOCV data, a possible graphic indication of progressive cell degradation during the cycle life test. The EOCV reflects the potential of the TiS_2 electrode, and a rapid rise in the EOCV is ostensibly due to problems at the cathode. A similar correlation between lithium transport in the cathode and capacity decline has been noted in the JPL cycle life studies (ref. 2). Low rate constant current charging as a reconditioning method is not effective. However, periods of open circuit stand after discharge may provide a reconditioning effect. The result may be due to reduction of temporary polarization conditions caused by operation at relatively high current density. Clearly, more work must be done to assess the effects of stand, self discharge, and reconditioning.

REFERENCES

1. Yen, S.P.S., Shen, D.H., and Somoano, R. B.: Elastomeric Binders for Electrodes. J. Electrochem. Soc., Vol. 130, No. 5, May, 1983, pp. 1107-1109.
2. Shen, D. H., Yen, S.P.S., Carter, B. J., and Somoano, R. B.: Lithium Diffusion in Secondary Lithium/ TiS_2 Cells. Proceedings of the Lithium Battery Symposium, Fall meeting of the Electrochemical Society, Oct., 1983.

Table I
Description of JPL Li-TiS₂ Cell

Configuration	Cylindrical - plates spiral wound
Capacity:	
Analytical Rated	0.63 Ampere-hours 0.48 Ampere-hours to 1.7 Volts
Voltage:	
Open.Circuit Load (Ave.)	2.7 Volts 2.0 Volts at C/3 rate
Number of Plates	2
Plate Area	77.4 square cm
Positive Plate	TiS ₂ on Ni Exmet-Elastomeric binder (ref. 1); no conductive diluent.
Negative Plate	Li Foil pressed on Ni Exmet
Electrolyte	(1.5M) LiAsF ₆ -2Methyl THF
Separator	2 Layers of Celgard 2400
Case Material	Stainless Steel
Size	2.3 cm diameter by 6.4 cm long
Weight	85 Grams

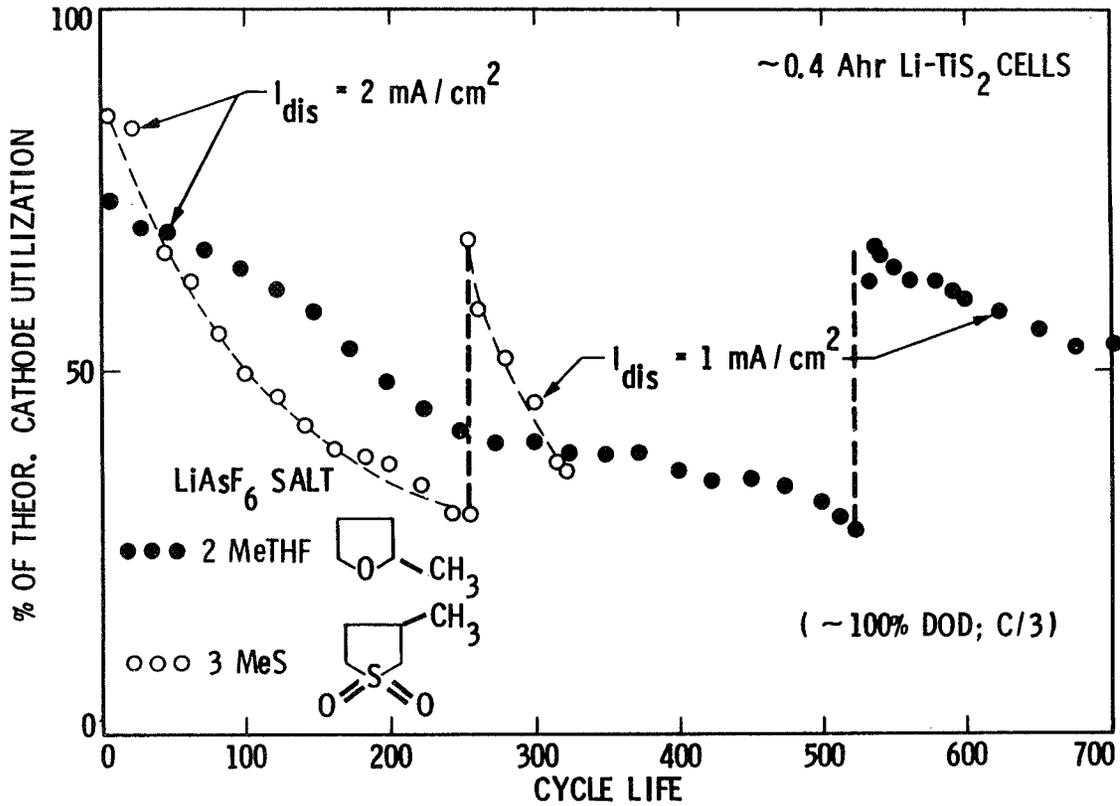
Table II
Annotation for Cycle Life Test

<u>CYCLE</u>	<u>NOTE</u>
1	To verify full charge at 2.64 volts and obtain rated capacity discharge.
2	To verify maximum start current, charge cut-off and rated capacity.
3	To determine voltage at 20% State-of-Charge (S.O.C.) cut off.
4	To determine voltage with 70% rated capacity return to 90% S.O.C.
23	High End-of-Discharge (EOD) voltage because computer malfunction caused 9 1/4 hour open circuit period during discharge.
61	First recondition charge (0.336 A-H return at 0.015 amperes).
66	Second recondition charge (0.396 A-H return at 0.015 ampere to 2.61 volts; and 0.384 A-H discharge).
72	Third recondition charge (0.387 A-H return at 0.015 amperes to 2.7 volts; and 0.384 A-H discharge).
73	Fourth recondition charge (0.387 A-H return at 0.015 amperes to 2.8 volts; and 0.384 A-H discharge).
75	Changed charge to discharge (C/D) ratio from 1 to 1.015 (0.336 A-H to 0.341).
78	Changed C/D from 1.015 to 1.03 (0.341 A-H to 0.346).
80	High EOD voltage because computer malfunction caused 9 hour open circuit period during discharge.
85	Changed discharge from 70% depth-of-discharge (D.O.D.) to 60% with 1.035 C/D ratio.
86	First open circuit stand recondition of 85 ^{1/2} hours between Cycle 85 EOD and Cycle 86 charge.
89	Started one hour delay after each discharge and start of next charge.
106	Changed discharge from 60% D.O.D. to 50% with 1.013 C/D ratio.

Table II
Annotation for Cycle Life Test (Cont.)

<u>CYCLE</u>	<u>NOTE</u>
109	Started one hour delay after each charge and start of next discharge.
119	Changed discharge cut-off voltage to 1.6 volts from 1.7 volts.
129	Open circuit stand recondition of 18 ^{1/2} hours between Cycle 128 E.O.D. and Cycle 129 charge.
138	Open circuit stand recondition of 74 hours between Cycle 137 discharge and Cycle 138 charge.

CELL PERFORMANCE



- LONGEST CYCLE LIFE REPORTED
- CAPACITY DECLINES WITH CYCLE LIFE - TWO DIFFERENT RATES
- LiAsF₆/2MeTHF YIELDS LONGER LIFE CYCLE THAN LiAsF₆/3MeS

Figure 1. Cycle life of a Li-TiS₂ cell.

BATTERY TEST STATION BLOCK DIAGRAM

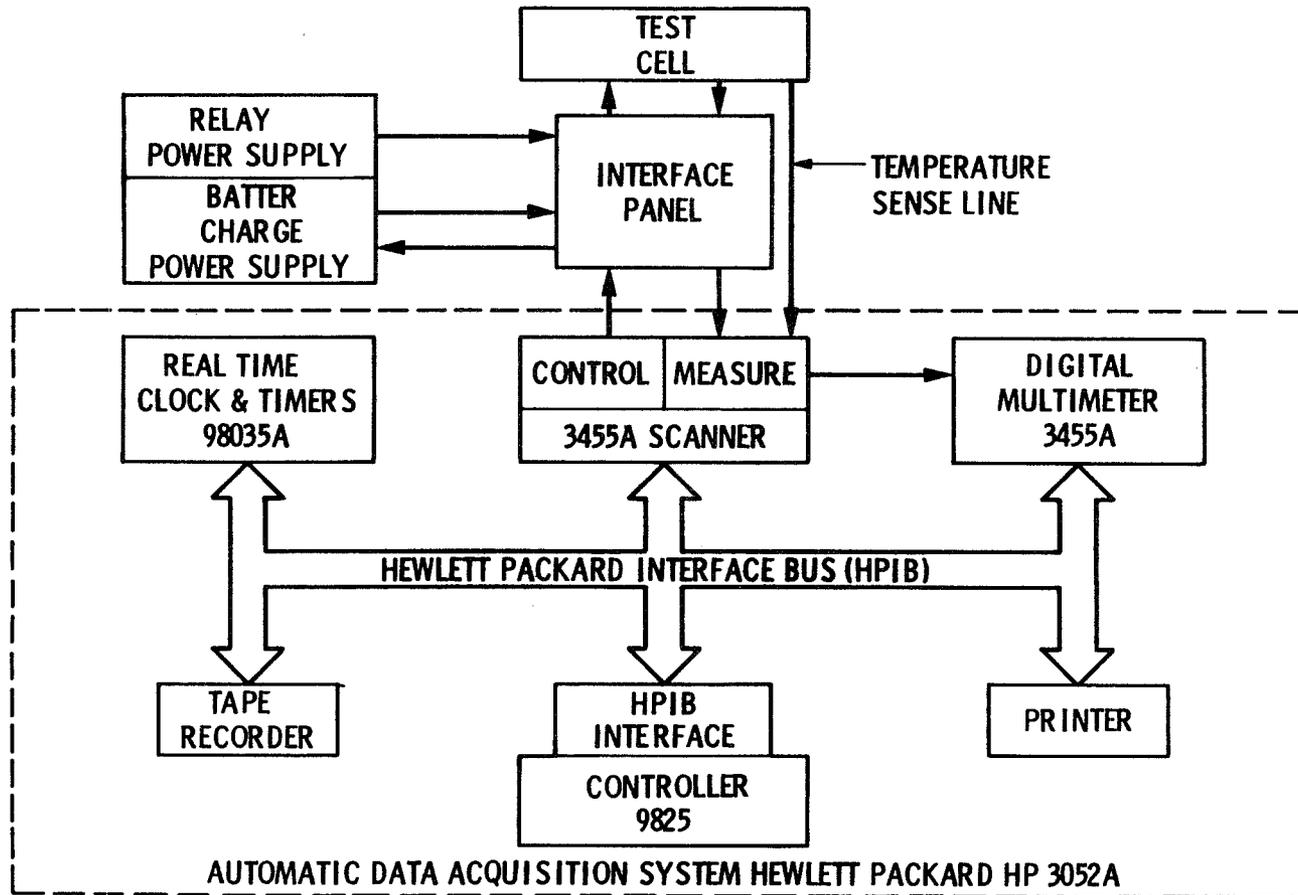


Figure 2. Battery Test Station Block Diagram.

CELL END-OF-CHARGE AND END-OF-DISCHARGE VOLTAGE VERSUS CYCLE (Li/LiAsF₆-2 MeTHF/TiS₂)

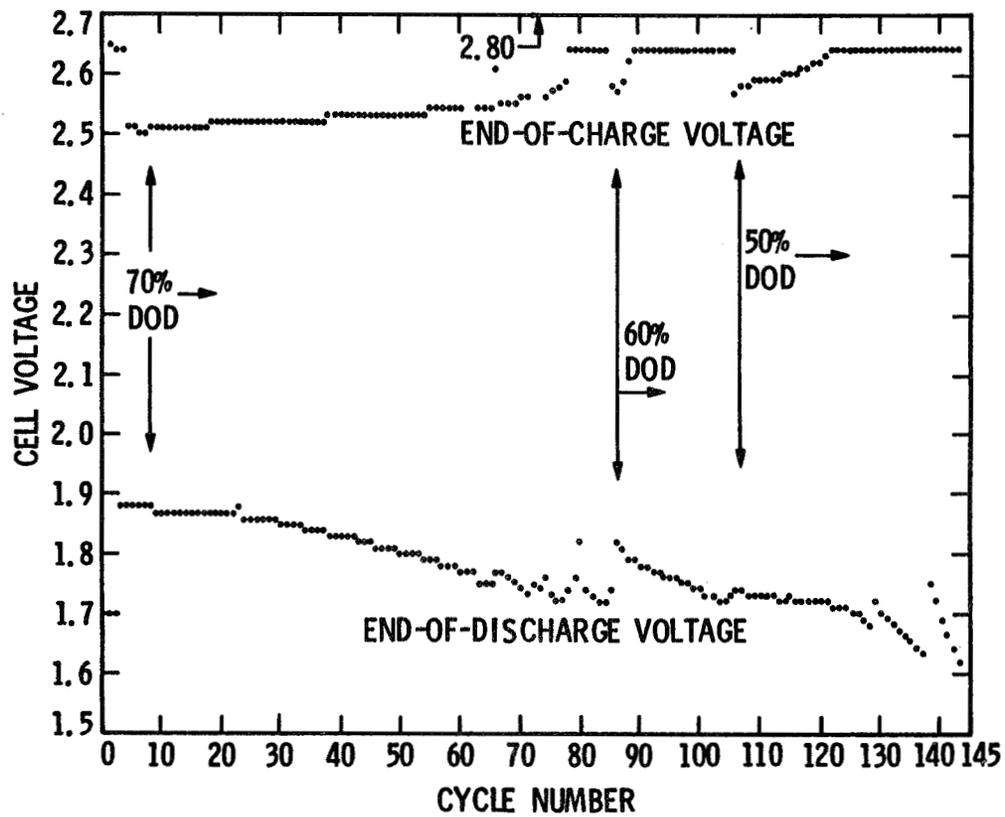


Figure 3. Cycle life test: End of charge and end of discharge voltage versus cycle.

TAPER CHARGE

CYCLE No.4 0.34 AMP hrs 0.81 WATT hrs

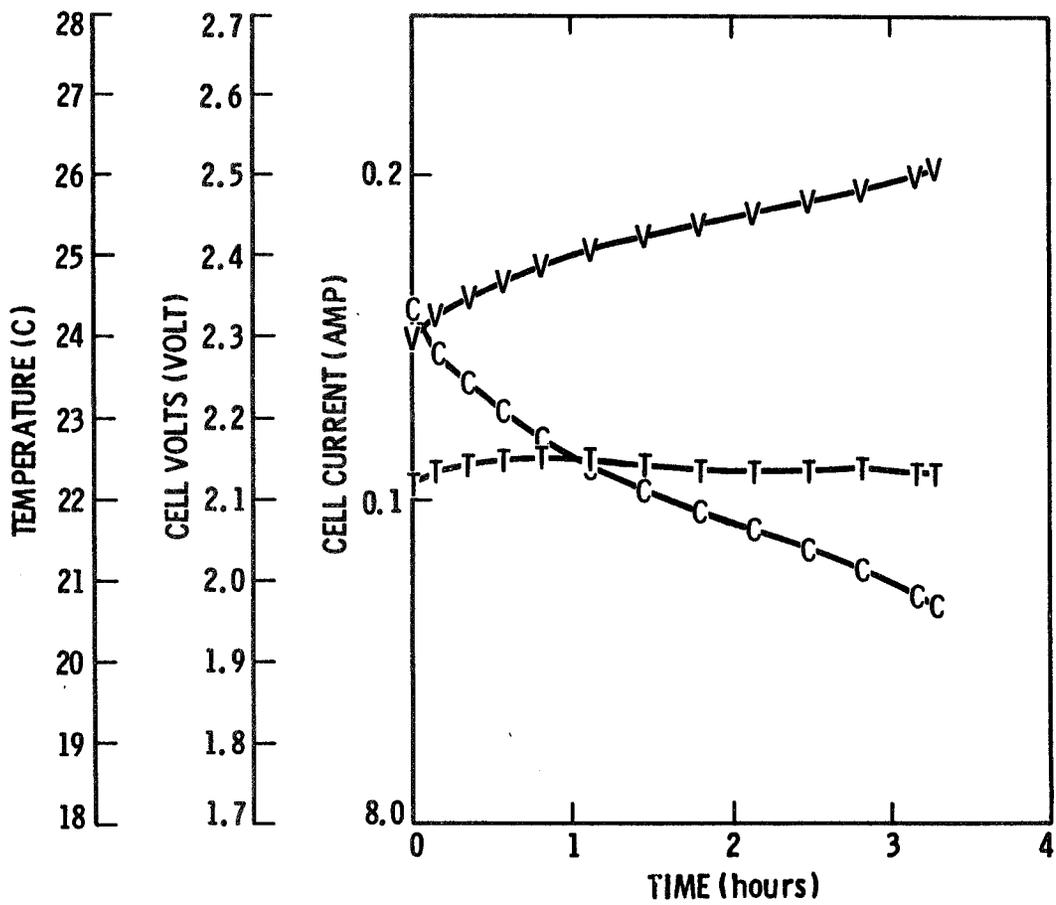


Figure 4. Charge Performance, Cycle No. Four.

DISCHARGE AT 0.155 AMPS
CYCLE No.4 0.34 AMP hrs 0.70 WATT hrs

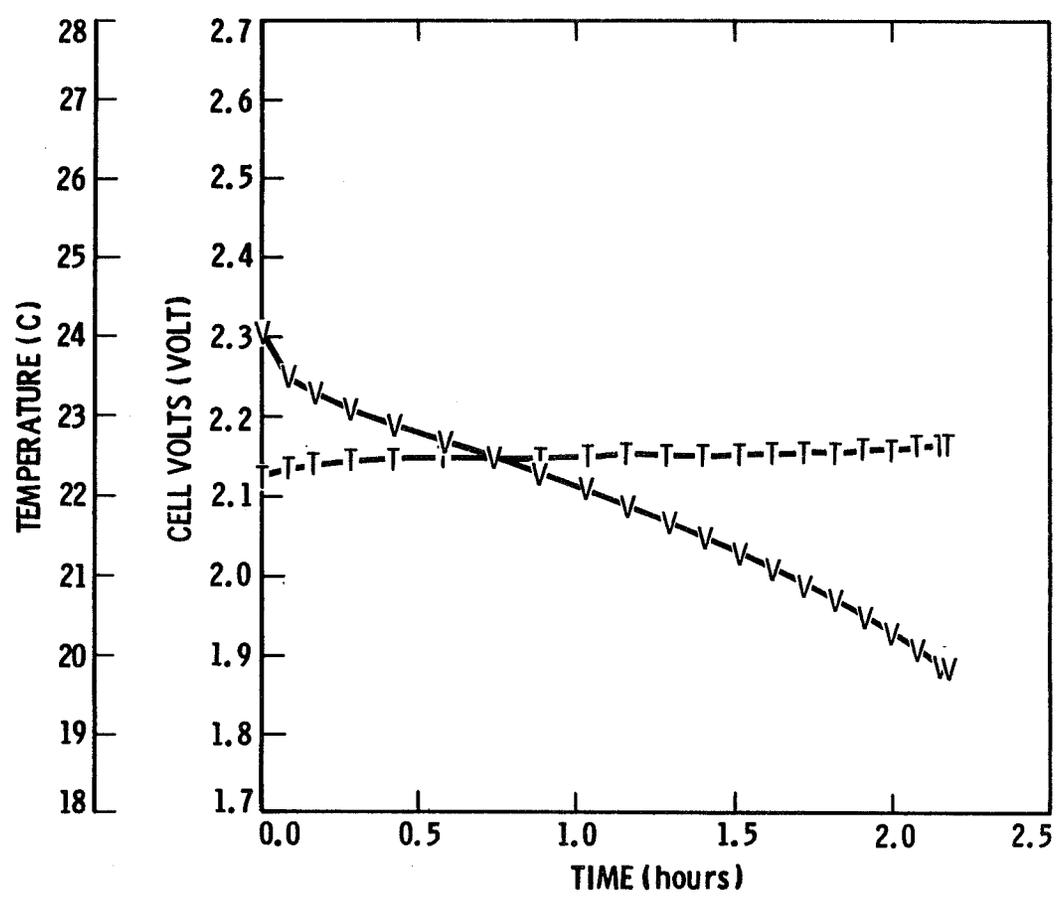


Figure 5. Discharge Performance, Cycle No. Four.

TAPER CHARGE
CYCLE No.84 0.34 AMP hrs 0.83 WATT hrs

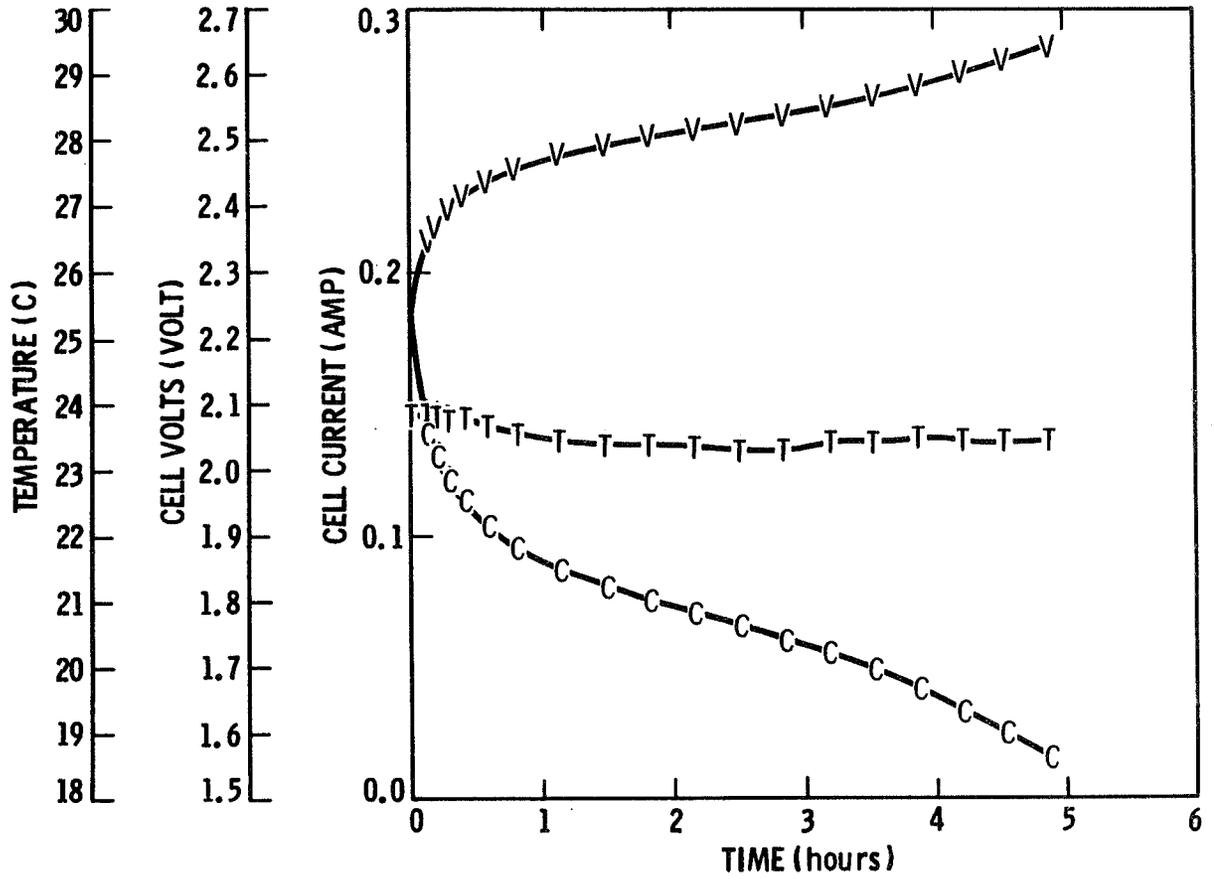


Figure 6. Charge performance, cycle no.84.

DISCHARGE AT 0.155 AMPS
CYCLE No.84 0.34 AMP hrs 0.66 WATT hrs

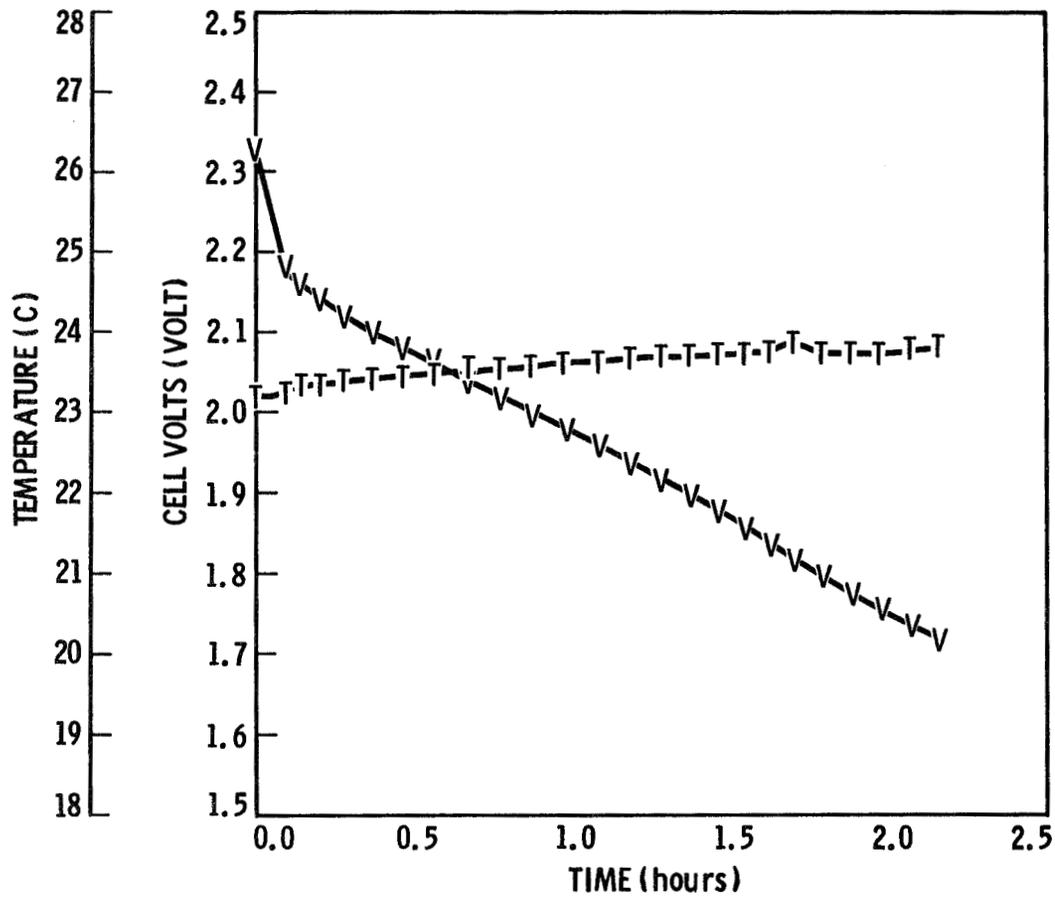


Figure 7. Discharge performance, cycle no.84.

SESSION II

DISCUSSION

- Q. Ritterman, COMSAT: You mentioned, I think you showed that the area of the electrode is about 80 square centimeters and you've got a current density of 2 milliamps per square centimeter. That's not your normal geosynchronous rate of discharge as say opposed to 10 or 12 milliamps per square centimeter. You've got roughly 12 square inches of area. It'll give you half an ampere of capacity. Is that particular to this laboratory cell or is this the way lithium cells are designed?
- A. Otzing, Rockwell International: No. It's just this particular cell. I think in the future they're planning on doubling that area. They really didn't try to do that. What you're saying I guess in effect is that what we're running like a three-hour rate and for synchronous you'd like to see more like a two hour rate.
- A. Ritterman, COMSAT: It's more than that. Two milli-amps per square centimeter is like I think a 410 discharge rate in NI-CD. I'm saying that probably you have to get a thicker electrode in order to make this thing feasible on the weight basis. So that your current density is lower than you would normally see. Two milliamps is lower than you'd normally see in geosynchronous discharge. It's something like 10 or 12 milli-amps per square centimeter.
- A. Otzing, Rockwell International: Well, like I said, I think that we're still early in the game and I think that it can be dealt with.
- Q. Ritterman, COMSAT: Do you have any data on thicker electrodes?
- A. Otzing, Rockwell International: No.
- Q. Ritterman, COMSAT: Does JPL have any data?
- A. Otzing, Rockwell International: The indication is no - by movement of the head.
- Q. Galassi, Hughes Aircraft: On one of your graphs you had a change in slope on your percent cathode utilization.
- A. Otzing, Rockwell International: Yes.
- Q. Galassi, Hughes Aircraft: You said you're investigating?

- A. Otzinger, Rockwell International: Yes.
- Q. Galassi, Hughes Aircraft: Is your cathode subject to pitting and therefore exposing more surface area causing change in slope?
- A. Otzinger, Rockwell International: I think that Dr. Somoano should answer that question.
- A. Somoano, JPL: When we used to use a teflon binder in our TIST cathodes yes, we had a problem with chemical integrity. Since we've been using the elastime binders the cathodes look very well. We don't see any profound pitting it all.
- Q. Dudley, European Space Agency: You mentioned you had an excess of lithium in the anode. Can you tell us roughly how much this documetric excess is and whether the loss is mechanical or a reaction with the electrolyte?
- A. Otzinger, Rockwell International: There is about a five to ten percent excess lithium and we think the loss is reactive with the electrolyte which is the major problem.
- Q. Allvey, Saft America, Inc.: This is more of the same question actually. Your original curve showed this loss of capacity down to about 50%. And I was actually wondering whether the cathode remained the limiting effect all throughout?
- A. Otzinger, Rockwell International: Yeah that's a very good question. We've taken these cathodes out of cells after several hundreds of cycles and put them in cells with fresh lithium, fresh electrolyte salt and so forth and found no improvement whatsoever in capacity. So we do think the cathode is being deactivated. However, it's very likely that problems with the lithium anode are giving rise to products that may be compromising the performance of the cathode. For example after many hundreds and hundreds of cycles we find some kind of entity permanently intercolated - irreversibly intercolated in the TIS 2. And these may be some of the degradation products of the lithium electrolyte reaction.
- Q. Harkness, NWSC: Bert, on your charge you mentioned on the taper charge - was it set up where the hardware was programmed as the cell voltage reached a certain point that the constant current would be stepped down? Or was that inefficiency in the power supply setting on a voltage limit to where it tapered early and then the voltage tapered on up to the charge voltage that you wanted?

A. Otzinger, Rockwell International: Let me see if I understand. We set up the taper charge parameters and they stayed in place. And then we superimposed the state of charge control parameters on top of that. And so that, when we started to go higher, eventually it got to where the state of charge of 70% we're putting in was greater than the capacity that was available in the cell - or it was getting there. And so it reached then as a final value, the constant voltage value that was set as part of the taper charge scheme. So you had really two charge control methods super imposed. We of course, would like to keep it out of control of the taper charge. We're just using the advantages of the taper charge method of putting in a relatively low rate of charge at the end, gain reducing the stress on a cell. That, of course is the one claim to fame of a taper charge. That's the only reason people do it. They can put a lot in when the cell is fully discharged and it wants to absorb a lot of charge and then put a lot less in at the end when it doesn't want to be taking a lot of charge on.

Q. Question inaudible.

A. Otzinger, Rockwell International: Okay that was the last one I showed. Cycle 84? Yeah, well I think what you're printing out is the fact when we are running out of capacity - then so, yes, you would drop down rather abruptly because you're running out of capacity.

COMMENT

Gross, Boeing: Since the purpose of this investigation was to obtain baseline information, I would think it would be worthwhile to conduct a further set of charge control investigations using lithium limited designs. For, after all, that's probably what you will ultimately want to have in a cell design, either by starting initially or eventually moving toward as a lithium electrode degrades.

Otzinger, Rockwell International: I guess we agree with you Sid.

Q. Myer, AT&T Bell Labs: We found that in order to get to anywhere near the practical densities of a lithium cell, that is higher than nickel cadmium, we had to reduce the amount of excess lithium substantially. And, under those conditions, the lithium became limiting electrode. My question is under those conditions would any of these charge control parameters be the same and do you have work in progress to look at the cycle life of the lithium electrode?

A. Somoano, JPL: That's a very good point. We've not looked at lithium limited electrodes and this is something we plan to do this fiscal year to initiate. I have no idea how the charge control procedures

- A. Somoano, JPL (Con't): would be and I might mention also, for higher energy density, we need to go to something other than TIS 2. It's merely a vehicle right now to assess the state-of-the art in electrolyte problems.