CHARACTERIZATION OF PROTOTYPE SECONDARY LITHIUM BATTERY

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I would like to discuss some of the work that is going on at JPL as a result of a new NASA-sponsored program which has recently been initiated on ambient temperature secondary lithium batteries.

(Figure 2-69)

The objective of the program is to develop improved ambient temperature lithium batteries from cells which would satisfy NASA's needs for energy density, safety, cycle life, etc.

By way of example, we are interested in energy densities of the order of 150 watts per kilogram or higher; cycle life of 200 to 500 cycles, or greater; make certain that life of battery is safe as possible, 5-to 10-year lifetime. These are the type of things we are checking for.

(Figure 2-70)

The type of system secondary lithium batteries that we are working on involves the use of an intercalatable cathode. These are based on the layered transition metal chalcoginides, such as titanium disulfide. You will be hearing some more of these talks following this one.

TiS_2 is much like graphite in that it crystallizes in layers, and the layers have been held together very weakly by van der Waals forces. One can make a battery out of this material with the lithium anode, suitable electrolyte and this layered structure as the cathode. Upon discharge, lithium ions can diffuse between the layers. The layers will open up and accept the lithium ions, and upon charge, the lithium can be removed back out with very little destruction and change of structure.

Indeed, one can do this over and over, and this is what one tries to exploit as a reversible cathode, which has an energy density of around 450 watt-hours per kilogram.

(Figure 2-71)

Well, the organization of the task here at JPL involved efforts focused on all components of the cell, anode, electrolyte, and cathode. This program is primarily a basic research program. That is, we are interested in gaining an understanding of the fundamental processes which can dominate and which can limit battery performance.

One aspect of this program is also a battery testing and evaluation. This reflects the fact that in a few years the basic research effort will tool down and be replaced by a prototype cell effort, in which they will be fabricating prototype cells in JPL for evaluation.

Prior to the initiation of this program in July, some cells have been purchased. Prototype cells have been purchased to evaluate at JPL. What I would like to do now is just discuss with you some of the very preliminary data, very preliminary in that I shall say we have tested three cells so far.

I think it will be interesting to you to be able to see the data we have obtained and to compare with some of the data you will hear in the next few talks.

(Figure 2-72)

So, as far as the evaluation of a prototype cell is concerned, what we are interested in is to try to find out just what would be the performance of a cell that we could go out and buy state-of-the-art cell, just to get a feeling of what type of performance characteristics one could expect. We wanted to identify the problem areas to see if there were any immediate near-term development needs and to make sure that these are being addressed by the basic research program as well.

The approach here was to go to a vendor – in this case, EIC in Newton, Massachusetts, and have him fabricate some lithium TiS_2 type cells for us. A typical type cell is shown right here. It is a prismatic cell.

EIC actually made two types of cells for us, D cells as well as prismatic cells. The D cells, we were alerted by EIC, had a contamination problem in which impurities ostensibly water in the TiS_2 cathode could possibly contaminate it, contaminating the lithium anode, and therefore lead to capacity fading.

The prismatic cells were made under much better conditions and were thought to be superior cells. These are hermetically sealed cells. We have essentially tested two of the D cells as well as one of the prismatic cells.

Since these are the first secondary lithium batteries that have been tested at JPL, the tests were done in their remote testing facility. What this results in is that we can only test a cell at a time so it is really quite slow.

So I will be showing you the results of testing two D cells and one prismatic cell. This work is currently in process and will be continuing.

(Figures 2-73)

The first vugraph right here shows a discharge curve for lithium TiS_2 cell. I should mention that the electrolyte in this material consists of a salt, lithium arsenate hexafluoride. The salt was 2

methyl KHF. These are ostensibly supposed to be about 5-ampere-hour capacity levels. That was one of the desired characteristics.

This is a discharge curve for a lithium TiS_2 cell. Notice that the discharge curve is about 300 milliamperes, so it is really quite low. But, indeed, that is what was used for the testing procedures.

JPL, as well as NASA, is certainly interested in higher discharge rates for the secondary lithium batteries, in particular C/1, C/1.5 type rates. But, initially to characterize this material, we used a 300-milliampere rate which is about the order of C/11.

If you look at these results, it corresponds to a capacity of about 3.4 ampere-hours if you use an average voltage of around 2 volts. You see it is about 57 watt-hours per kilogram in this particular cell. This is the first cycle, the first discharge.

We have done some ID characteristics down near the fully discharged region, as shown in the next vugraph.

(Figure 2-74)

This is the voltage versus current. As you can see, from the right is discharge; from the left is charge.

Nothing really unusual is seen here. It is a typical behavior that we expect. This indicates there is no other type of adverse reaction occurring, at least within the current voltage range that we have been looking at.

(Figure 2-75)

On the next vugraph we will show you a typical charge cycle. Again, it is used at 300 milliamperes. A couple of features I would like to point out here. It is quite similar to the discharge curve. It is a little higher voltage. But, you will notice a sharp upturn near the fully charged state.

We don't know what is causing it to turn up like that. It is something that can be used as control point possibly. We have terminated the test at 3 volts as well as 1.6 volts, and these are the recommended cutoff voltages as suggested by EIC.

We have done some IV characteristic tests right near the fully charged region, which is shown on the next vugraph.

(Figure 2-76)

They are really quite different from the fully discharged state. Again, for discharge situation, there is not much change, but as you notice when we charge, especially above 3 volts, there is quite

high voltages being generated. We don't really know what is the cause of it. It has been suggested to us by EIC that what may be happening is electrolyte degradation here, in particular polymerization reaction. In any event, this is one of the areas we will be interested in to see what is happening in these regions.

(Figure 2-77)

The next vugraph shows load capacity versus cycles. I would like to call your attention to the solid line first. Again, this is the first D cell tested. You see roughly about 3-ampere-hours capacity to about the 15th cycle. After that the capacity drops fairly rapidly; it is essentially zero about the 21st cycle.

We tested the second D cell, and it essentially followed the behavior of the first. At about the 5th cycle it ruptured. Again, we feel that this probably reflects the fact that there was moisture, water in these materials. However, we don't know completely what is the cause of the problem.

We have looked at one of the prismatic cells which are from one of the better batches. The second batch you can see out here. Essentially it starts out at about 3-ampere-hour capacity, rises to about 4 ampere-hours, and stays constant to about the 18th cycle. I don't have the actual data here. Beyond the 18th cycle, one can no longer charge it. There is quite a bit of evidence of shorting occurring in all these materials.

(Figure 2-78)

So, let me summarize the conclusions that we have found in this very limited test. Certainly the cycle life of lithium anode is a very important problem. We need a lot more cycles than this. This is an area where we think we can make some progress. It is an area where JPL will be focusing quite a bit of attention.

The impurity control is critical. That is obvious. Everyone knows that. I think this data may reflect just how it can affect some of the performance of the secondary lithium-type cells. One of the main type of failure mechanisms or failure modes, we believe, that is occurring here is the formation of dendrite breakage and subsequent shorting.

DISCUSSION

GROSS: EIC has been successful with considerably more cycle life on some cell designs than the one that you tested. Has it not been determined what the differences were?

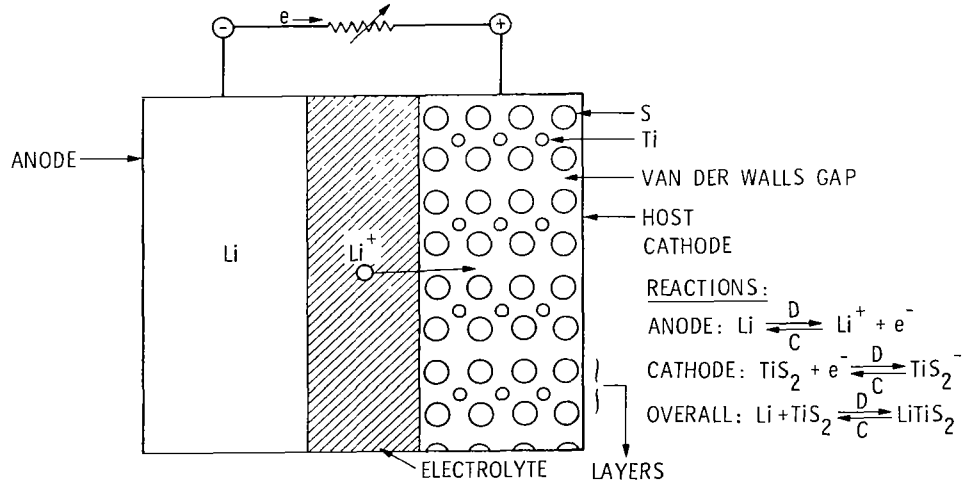
SOMOANO: I think there were problems with the scaleup, and probably Gerhart may address some of these questions in his talks. They certainly got much more cycle life in laboratory cells than in smaller cells.

OBJECTIVE

TO DEVELOP IMPROVED AMBIENT TEMPERATURE SECONDARY LITHIUM BATTERIES WHICH WILL SATISFY NASA's FUTURE NEEDS FOR ENERGY DENSITY, CYCLE-LIFE, AND SAFETY

Figure 2-69

SCHEMATIC DIAGRAM OF A SECONDARY Li/TiS_2 BATTERY



DISCHARGE . . . . . INTERCALATION (INSERTION)
CHARGE . . . . . DE-INTERCALATION (REMOVAL)

Figure 2-70

SUBTASKS

- ANODE SUBTASK
- ELECTROLYTE SUBTASK
- CATHODE SUBTASK
- BATTERY TESTING AND EVALUATION SUBTASK

BASIC RESEARCH PROGRAM INVOLVING STUDIES OF FUNDAMENTAL ELECTROCHEMICAL PROCESSES

Figure 2-71

EVALUATION OF AMBIENT TEMPERATURE SECONDARY LITHIUM PROTOTYPE CELLS

OBJECTIVE

- TO DETERMINE PERFORMANCE CHARACTERISTICS OF STATE-OF-THE-ART PROTOTYPE CELLS
- TO IDENTIFY PROBLEM AREAS, NEAR-TERM DEVELOPMENT NEEDS, AND AREAS REQUIRING FUTURE BASIC RESEARCH

APPROACH

- EIC FABRICATED PROTOTYPE CELLS FOR JPL EVALUATION
  - CELLS – Li/TiS_2 W/$LiAsF_6$ AND 2-Me-THF AS ELECTROLYTE (~5A-HR DESIRED CAPACITY)
  - EVALUATION – CONTINUOUS CYCLE TEST W/PERIODIC I-V MEASUREMENTS

Figure 2-72

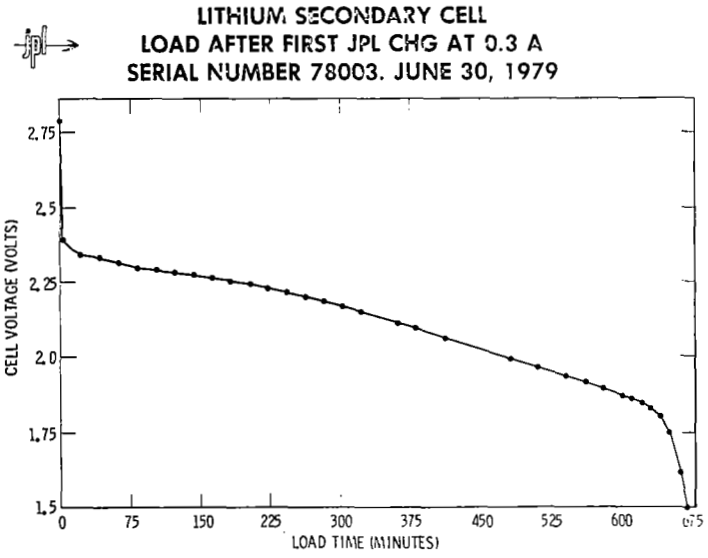


Figure 2-73

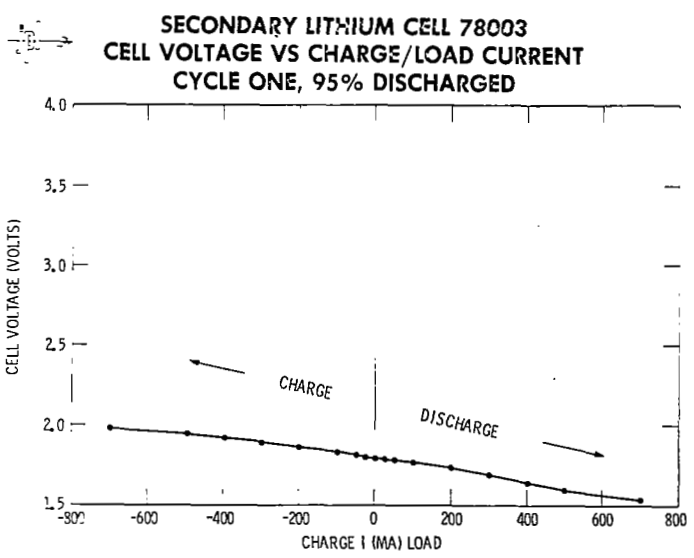


Figure 2-74

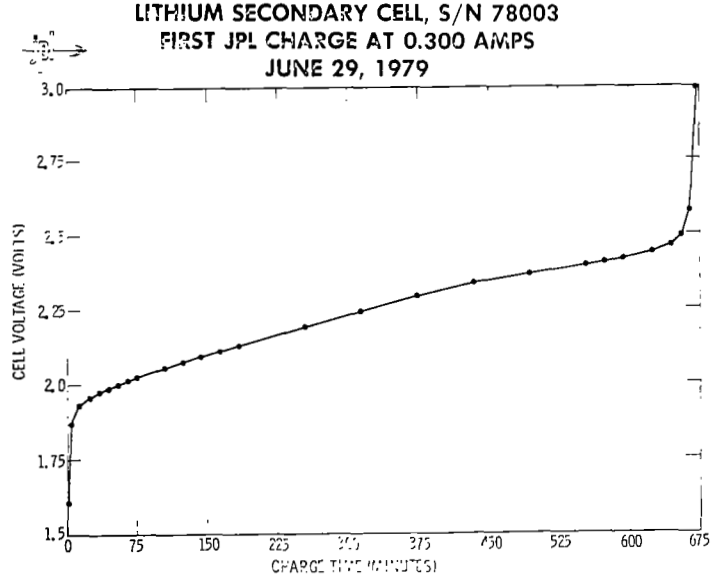


Figure 2-75

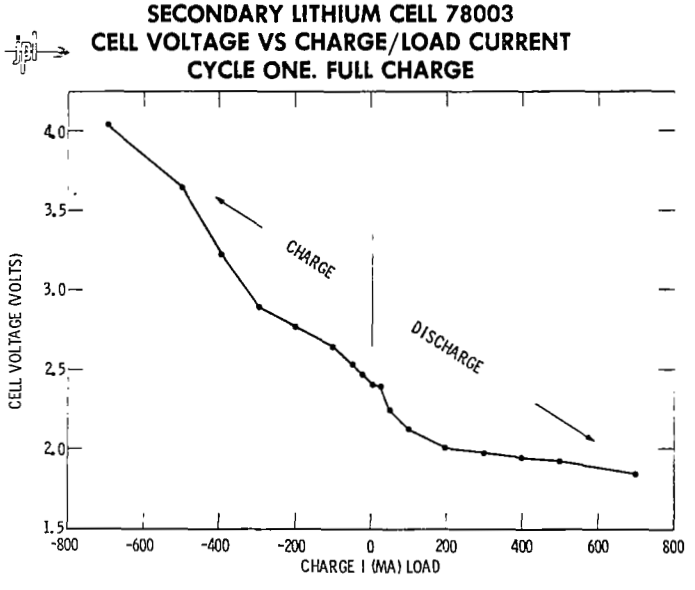


Figure 2-76

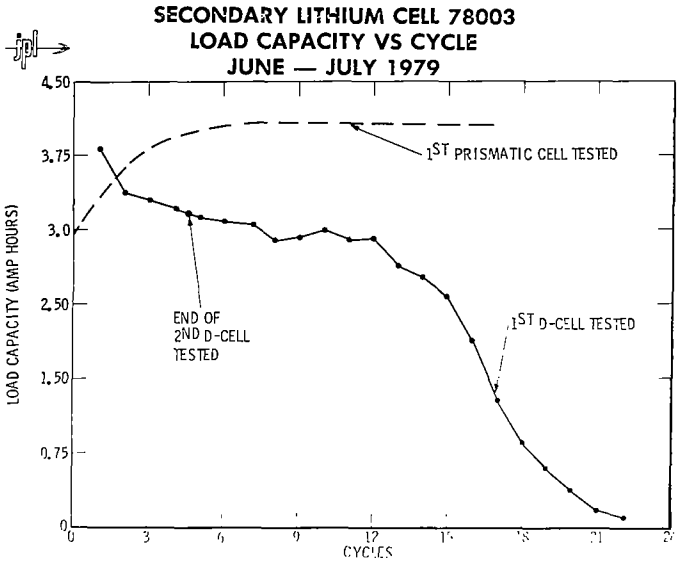


Figure 2-77

CONCLUSIONS

- CYCLE LIFE OF THE LITHIUM ANODE IS AN IMPORTANT PROBLEM AREA
- IMPURITY CONTROL IS CRITICAL
- FORMATION OF SHORT CIRCUITS UPON CHARGE, DENDRITE BRIDGING, IS AN IMPORTANT FAILURE MODE
- ENERGY DENSITY CAN BE INCREASED BY USING MORE EFFICIENT CATHODE STRUCTURES

Figure 2-78