

RECHARGEABLE AMBIENT TEMPERATURE LITHIUM CELLS

G. Holleck
EIC

As you have heard today, there are a number of very attractive primary cells already available today. With secondary cells, progress has been somewhat more gradual.

At EIC, we have devoted a considerable effort over the past years in developing ambient temperature lithium cells, in particular, in solving the problem that is common to all secondary lithium cells, which is cycling of the lithium electrode.

Now, the high reactivity of lithium requires very nonreactive solvent. Several solvents appear to be stable if you store lithium in them. This stability is not a thermodynamic stability, but it is a kinetic stability.

You have protective films on the lithium surface which inhibit the reaction. In general, the problem is that you cannot cycle lithium very well in these conditions.

(Figure 2-79)

Let us quickly review what the problems actually are. You can plate lithium quite efficiently out of menthols with 100-percent efficiency. The problems are that the deposit has a bad morphology and comes out dendritization and passivates on stand. Especially on cycling, the efficiency deteriorates rather rapidly.

(Figure 2-80)

In this figure I have indicated a schematic so you can view what happens. But, in plate lithium you plate fresh lithium which covers itself with a protective layer consisting of electrolytes and reaction products with the electrolyte. Some parts might become encapsulated and thus isolated from the substrate.

When you subsequently strip the deposit, part of the lithium will dissolve and part will remain at the electrode. So your stripping efficiencies are less than 100 percent. When you continue the cycle, you accumulate more and more of such isolated material at the surface, and your surface morphology continues to degrade.

This material is predominant with lithium if you analyze it. It is still lithium, but in a form that you cannot get access to by stripping.

(Figure 2-81)

Now, we have approached the system, this problem, in several ways. Let me just point out the two most successful approaches.

We found out that lithium heptofluorarsenate is the best salt precursor that we have found in any electrolyte so far. The reason for this is the reactivity of the salt and the formation of a protective film which has beneficial properties. Most of our experiments have been carried out in THF, which perform better than many other solvents we have looked at.

However, THF heptofluorarsenate solutions are still too reactive for practical secondary batteries. So, the second approach that we took was to modify the ether solvent, in this case, by introducing methyl groups in the alpha position and making it less reactive in this way.

So we relied on a 2-methyl THF: lithium heptofluorarsenate electrolyte as our best present electrolyte for secondary lithium cells; electrolyte preparation, naturally, as a big influence on performance.

(Figure 2-82)

Now, let me quickly show you in the next three figures two items which illustrate the behavior of the lithium electrolytes. These are half-life studies made by Cook in our laboratory.

Here you see, for example, a storage test of lithium and various electrolytes. I would just like to point out that in the type of THF you see a matter of various days depending on preparation methods. In the 2-methyl THF in excess of 10 months of the year, we have not seen any degradation. This is storage. By the way, the temperature is at 71°C.

(Figure 2-83)

This gives you a comparison of cycling efficiency of the lithium electrode as a function of cycle number. In the figure you see typical decay of THF and the much better performance of the 2-methyl THF.

(Figure 2-84)

Another aspect which is important for practical batteries is the reaction of lithium in the electrolyte on open circuit stands. Again, I show you some data comparing THF and 2-methyl THF. After 48 hours, the plated THF has completely reacted or is not accessible by stripping, which does not mean reaction or encapsulation. The 2-methyl THF is still accessible.

There are a few other points that I like to point out. There are areas where we get clearly a larger amount of capacity back than we had before. This is a phenomenon which is very important also for secondary batteries and which we call recontacting. Some of the material that previously had been isolated can be recontacted and can be regained. This is of great practical importance.

(Figure 2-85)

Now, with these data, we were very encouraged to go on and to look at full cells. We built prototype cells with various configurations, button cells, D-size cells, and prismatic cans as you have just heard before with cathodes of the intercalation type, titanium disulfide, chromium vanadium disulfide, and vanadium oxide, V_6O_{13} .

Common to all of these cathodes is that they intercalate lithium reversibly without decomposition of the host structure.

(Figure 2-86)

This shows you typical cycles for titanium disulfide, lithium titanium disulfide cell. As you can see over the cycles, the general shape, the discharge curve which is characterized by a slightly sloping plateau at a voltage of about 2 volts does not really change much. Actually it decreased somewhat. The curves have not changed.

The upturn at the end, these are cathode limited cells and on charge the increase in voltage. So, you get the voltage increase, and you would get this until some other reaction naturally will take over eventually. But it is fairly distinct.

Let me say one other thing. Most of our long-term testing has been done with titanium disulfide cells, and maybe I should first look at the next two figures.

(Figure 2-87)

This is a typical charge-discharge curve for a lithium vanadium disulfide cell. It is characterized by a similar slightly sloping discharge at about 2.4 volts, higher voltage than the titanium disulfide and similar type of charge.

(Figure 2-88)

This is a discharge charge of a lithium vanadium oxide cell. Here you have actually three plateaus; one less than the one up here, 2.5 volts, and at about 2.2 volts, and on charge followed the same multistep process.

(Figure 2-89)

Now, most of the extensive cycling has been carried out with titanium disulfide cells. The cycle regime that we have used consists of full depth cycles between preset voltages, 1.6 volts on discharge, for example, and 3 volts on charge at about the 6-to 10-hour rate.

This is somewhat different from what you normally do in cycle testing of conventional cadmium cells. They constitute a much more severe cycle regime. I have summarized some cycle results from small cells. These are naturally cathode-limited cells, and you see a slight decrease in capacity with cycle number.

For example, we have reduced the column density by half, and the capacity has come up to the initial value which is a clear indication that the cathode structure is the main determining factor here, not the decomposition of the cathode material. But a change in cathode structure produces this activity.

(Figure 2-90)

Now, having shown that you can cycle such cells, it naturally becomes interesting at what performance you can expect from realistic cell configurations. Using realistic cathode, formulations, and packaging, I have calculated here energy densities for E-size cells, and I have plotted it as a function of the lithium anacode efficient, which was naturally a very important factor for two different cathodes. In the cathodes, naturally the degree of cathode utilization is an important factor in determining your energy density.

You get these type of curves where you see that with a titanium disulfide cell, you can expect somewhere between 80 and 140 watt-hours per kilogram. With a lithium vanadium oxide cell, the range is somewhat larger from about 110, 120 to almost 300 watt-hours per kilogram.

It is interesting to note that a lithium electrode deficiency naturally plays a role in all of these cells, but it comes in much more strongly if you go to a higher energy density cathode. There it makes a large difference on what your electrode performance actually turns out to be.

(Figure 2-91)

This shows the same type of effect on radiometric energy density, and here again you cut off, depending on the lithium electrode efficiency for titanium disulfide to a range of about 180 to almost 400 watt-hours per liter and for the vanadium oxides, 210 to somewhere up here.

(Figure 2-92)

Now, let me summarize the status of the secondary lithium cells.

Two-methyl THF lithium heptafluorarsenate has shown the best cycling performance to date, and it has exhibited excellent behavior on stand.

Laboratory cycling results were verified in complete cells, so we think the feasibility of a lithium titanium disulfide cell, for example, with a cycle life of 100 cycles, have been demonstrated.

Practical cell configurations have attractive energy densities, between 80 and 290 watthours per kilo, and 175 to 800 watthours per liter, depending on the system, specific system.

DISCUSSION

BROADHEAD: How many ampere-hours of lithium did you use in your D cells and your prismatic cells?

HOLLECK: Well, we have built a number of cells, and it naturally depends on what cycle life you design the cell for; how much more you put in. In the small cells that I have shown you, the lithium efficiency is in the mid-90 percent. I don't quite remember how much lithium is in the large cells, 10-mil electrodes, and I have to calculate what that comes out to be with the specific capacities.

WHAT ARE PROBLEMS WITH RECHARGING
LITHIUM ELECTRODE?

- PLATING EFFICIENCY $\sim 100\%$ BUT STRIPPING EFFICIENCY $< 100\%$.
- DEPOSIT DENDRITIC.
- DEPOSIT PASSIVATES ON STAND.
- EFFICIENCY OF DISCHARGE DETERIORATES ON EXTENDED CYCLING.

Figure 2-79

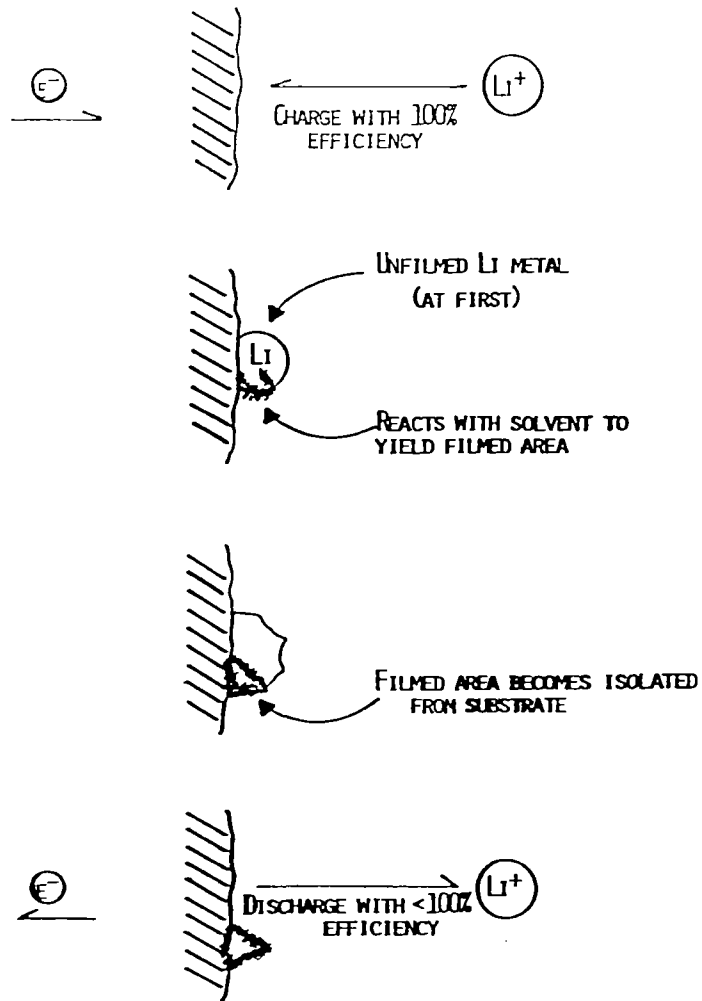


Figure 2-80

IMPROVED Li CYCLING

- LiAsF_6 BEST PRECURSOR
- MODIFIED ETHER SOLVENT (2ME-THF)
- ELECTROLYTE PREPARATION

Figure 2-81

THE ONSET OF Li REACTION WITH CYCLIC ETHER BASED ELECTROLYTES AT 71°C

PURIFI- CATION PROCEDURE	1M LiAsF_6 / THF	1M LiAsF_6 / 2-ME-THF	1M LiC_2O_4 / 2-ME-THF	1M LiAsF_6 / 3-ME-THF	1M LiAsF_6 / 2,5-DI-ME-THF
NONE	2(16) ^a	-	-	-	-
A ^b	25(28)	13 Mo	-	-	-
DAPA ^c	4(7)	>10 Mo	6 Mo	10(4)	12 Mo

^aOBSERVABLE Li CORROSION AFTER 2 DAYS; OBSERVABLE ELECTROLYTE COLORATION AFTER 16 DAYS.

^bSOLVENT PASSED THROUGH ALUMINA.

^cSOLVENT DISTILLED; PASSED THROUGH ALUMINA; SALT ADDED IN THE COLD FOLLOWED BY PREELECTROLYSIS; ELECTRODE PASSED THROUGH ALUMINA.

Figure 2-82

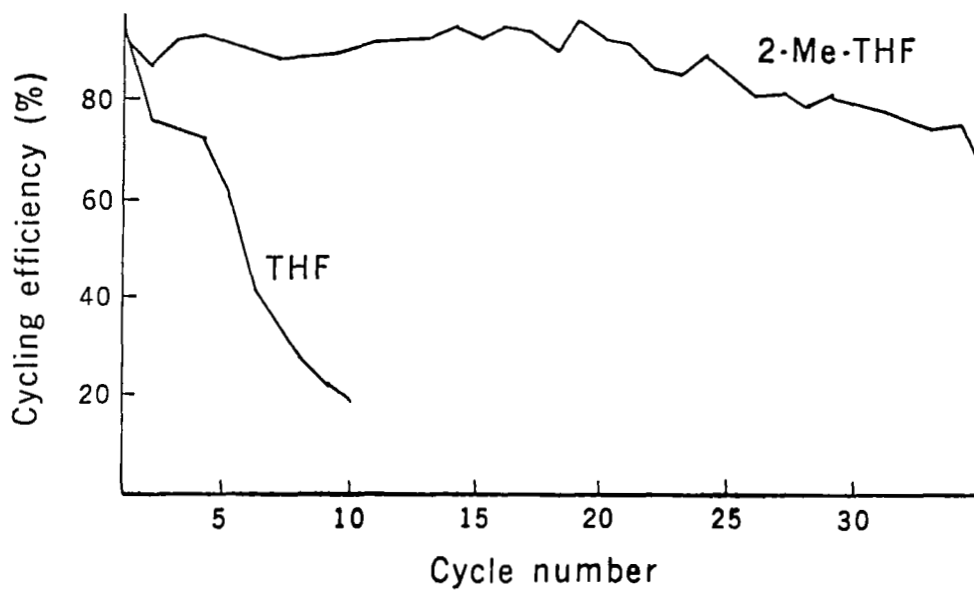


Figure 2-83

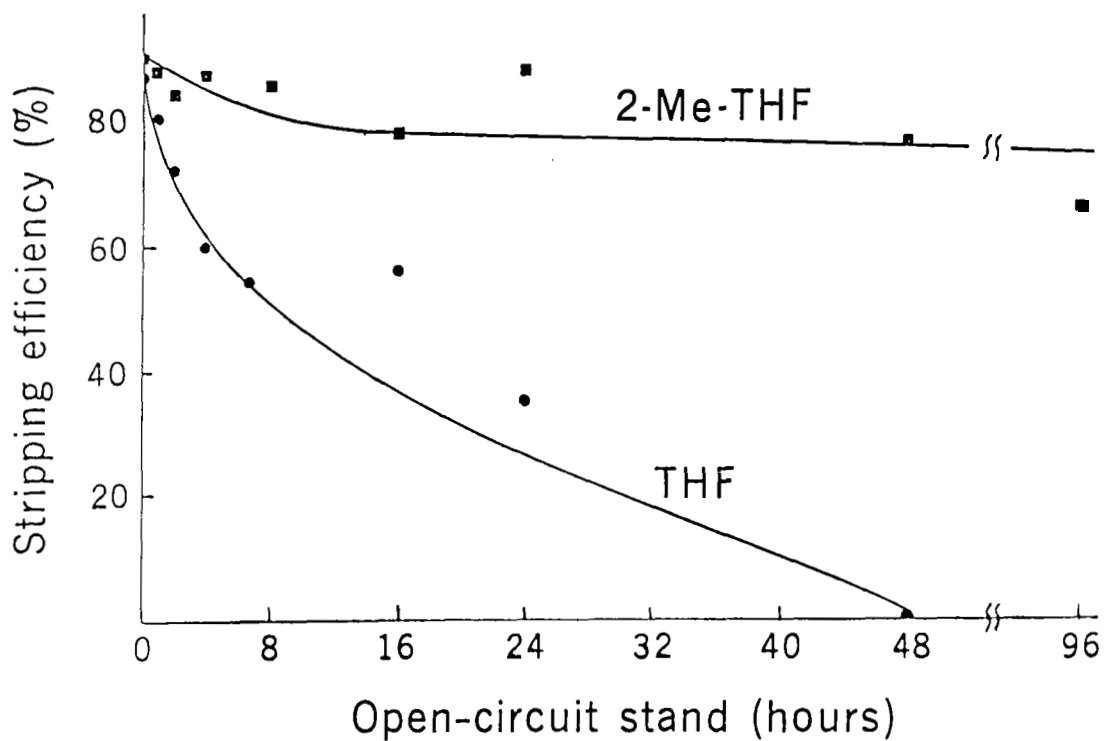


Figure 2-84

PROTOTYPE CELLS

- CATHODES: TiS_2
 $\text{Cr}_x\text{V}_{1-x}\text{S}_2$
 V_6O_{13}
- CONFIGURATIONS: BUTTON CELLS
D-SIZE CANS
PRISMATIC CANS

Figure 2-85

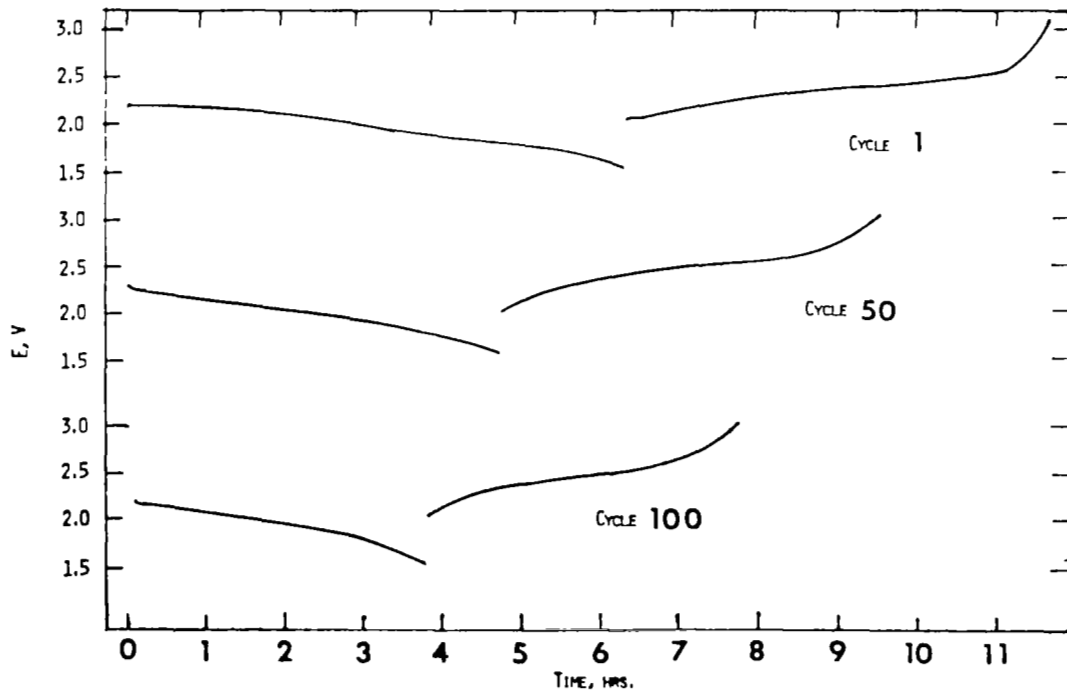


Figure 2-86

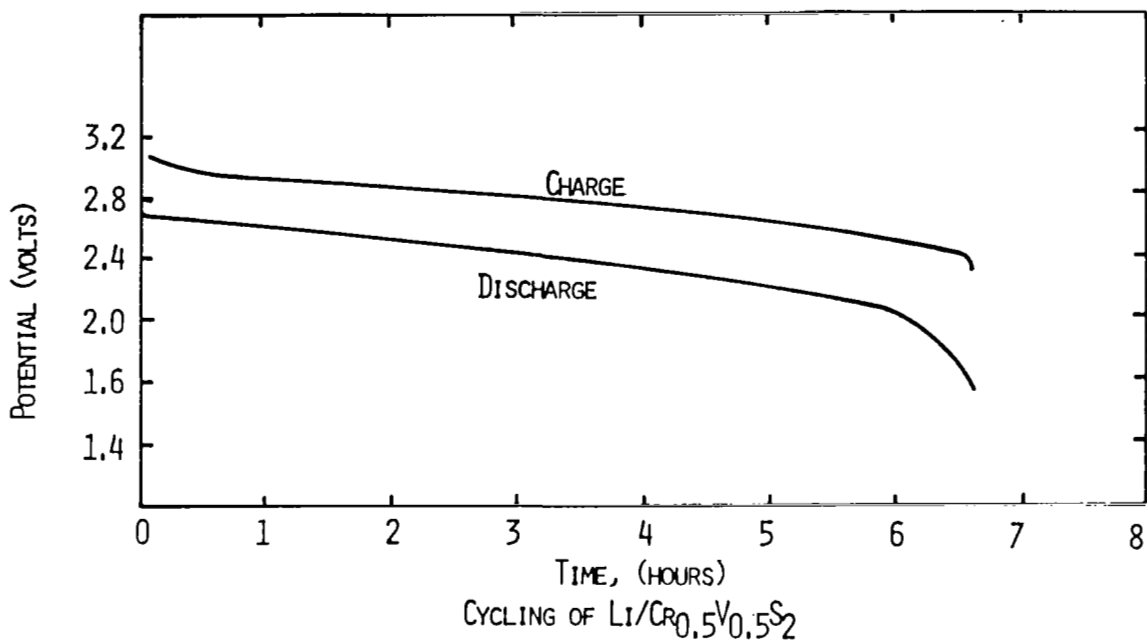


Figure 2-87

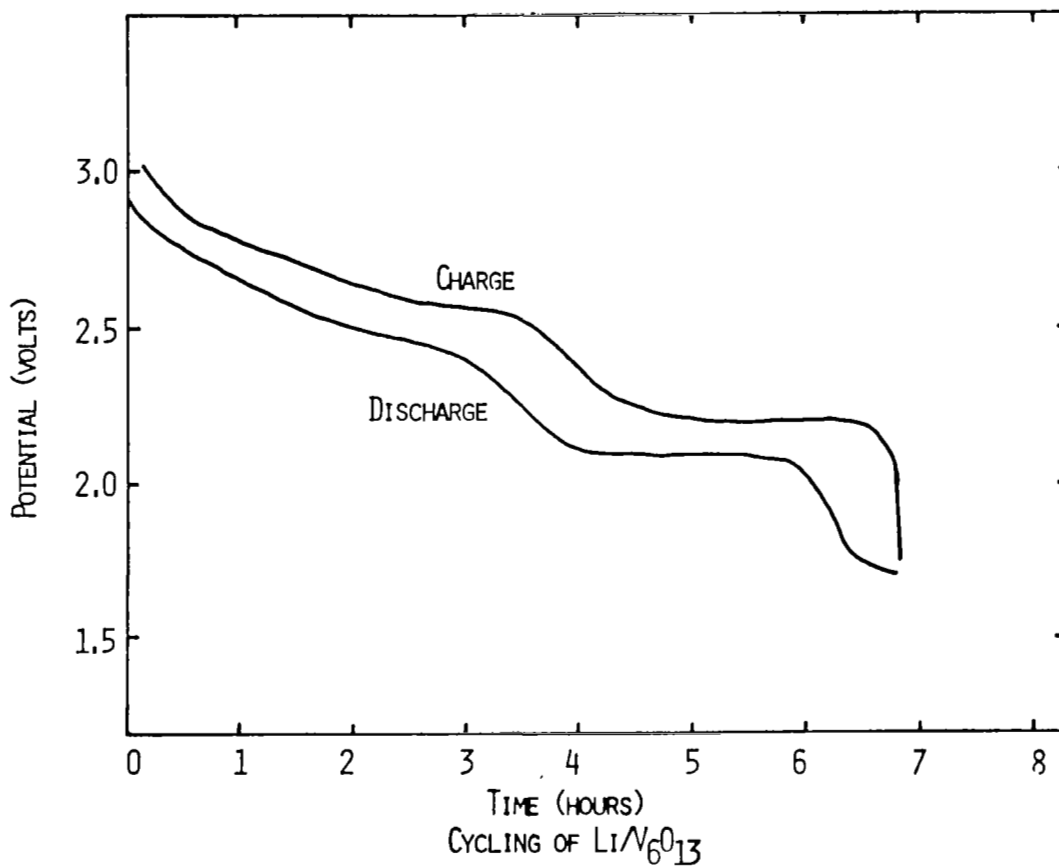


Figure 2-88

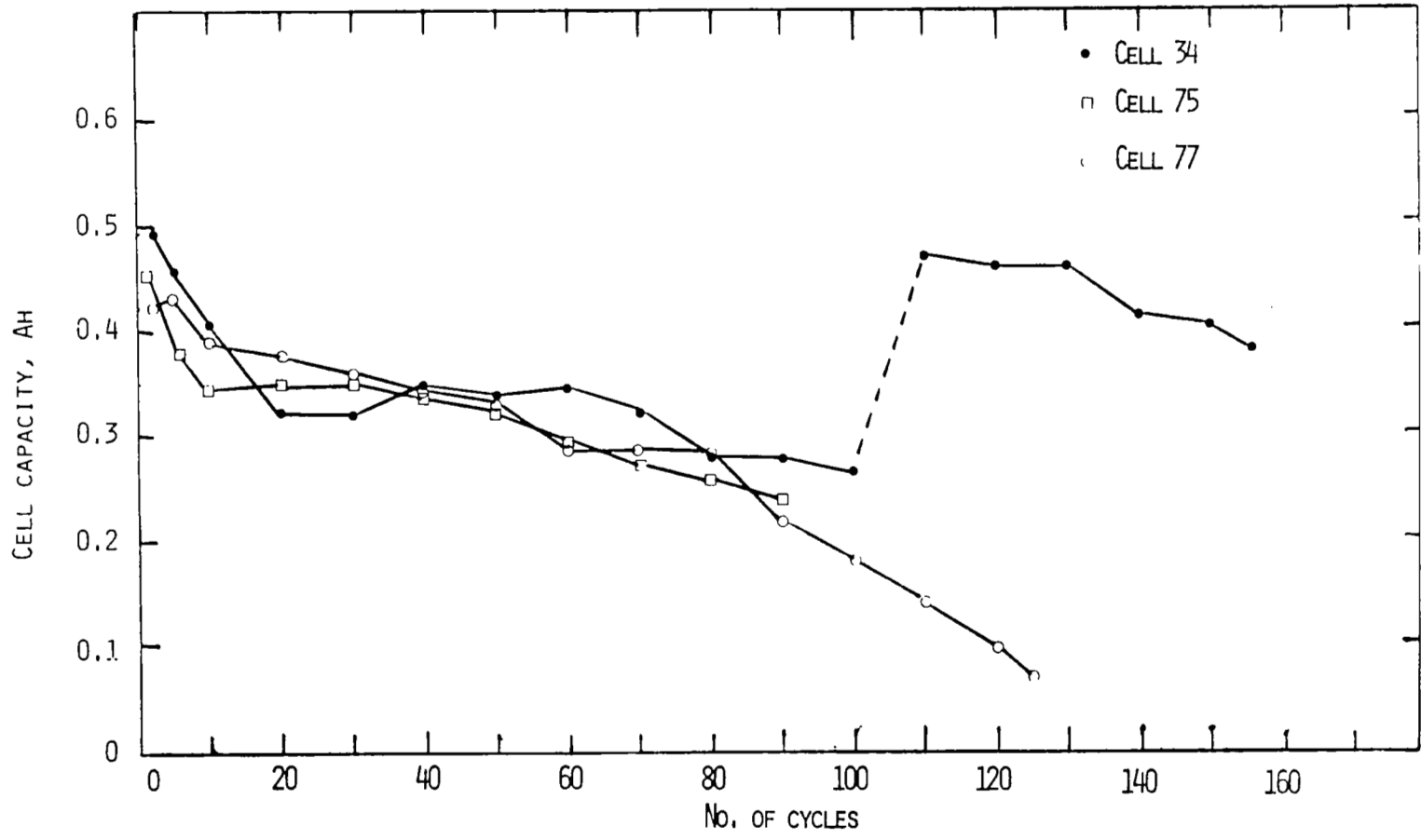


Figure 2-89

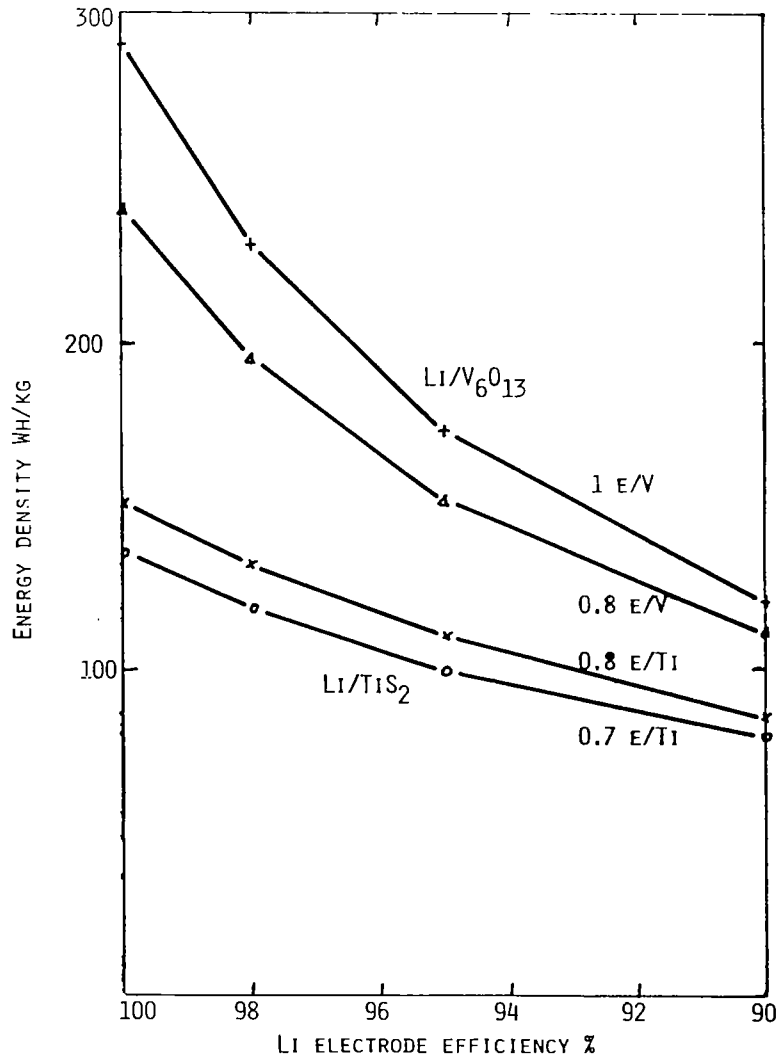


Figure 2-90

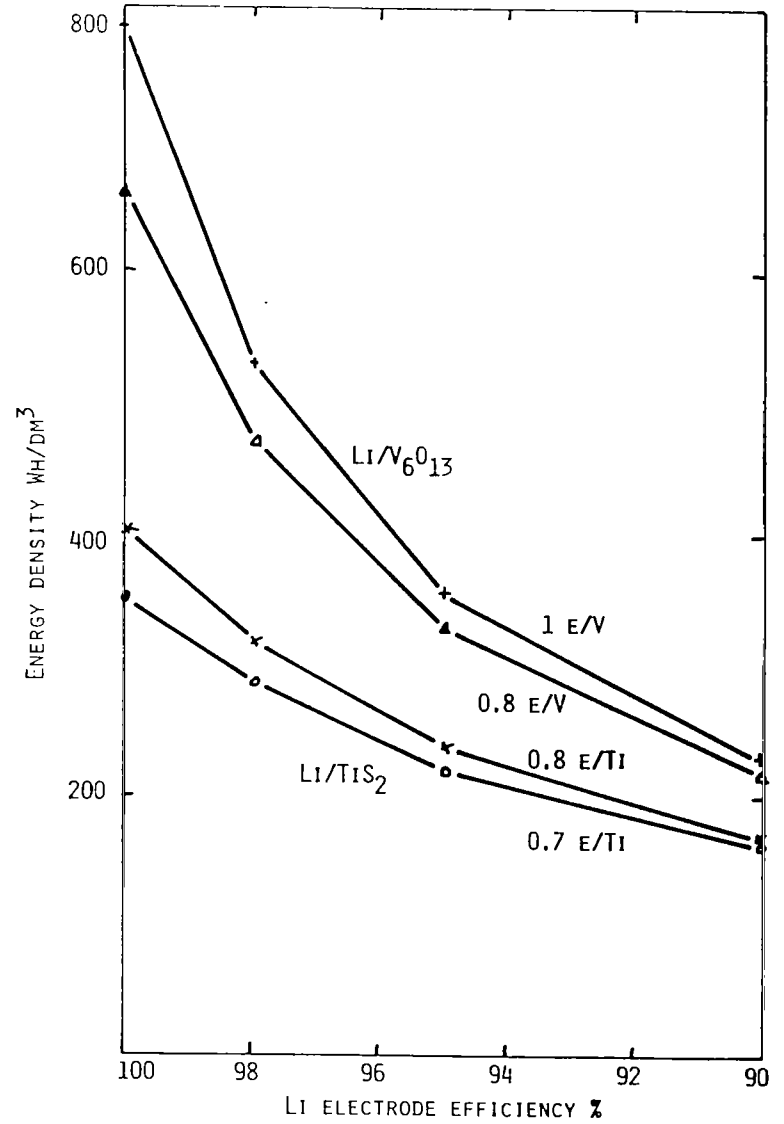


Figure 2-91

STATUS OF SECONDARY LI CELLS

- 2ME-THF/LI/AsF₆ SHOWS THE BEST CYCLING PERFORMANCE TO DATE. EXCELLENT BEHAVIOR ON STAND.
- LABORATORY CYCLING RESULTS VERIFIED IN COMPLETE CELLS.
- FEASIBILITY OF 100 CYCLE LI/TIS₂ CELL DEMONSTRATED.
- PRACTICAL CELL CONFIGURATION HAVE ATTRACTIVE ENERGY DENSITIES (80 TO 290 WH/KG, 175 TO 800 WH/l)

Figure 2-92