

LITHIUM THIONYL CHLORIDE HIGH RATE DISCHARGE

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For the past three years, GTE has been involved in a program of research and development in the area of high rate lithium thionyl chloride power technology. This afternoon I want to quickly review the results of this for you.

(Figure 2-41)

The figure contains a listing of the four main parameters we have identified by which you can control the high-rate performance characteristics of this cell.

They include the electrolyte composition, the operating temperature, cathode design, and the cathode composition. And I am going to talk about each of these parameters one at a time, beginning with the operating temperature.

The results I am going to be showing you are obtained with experimental laboratory cells, and our purpose is to determine the range of the limits of improvement that we can obtain in high-rate performance by the variation of these parameters.

(Figure 2-42)

The next slide contains some polarization curves. This is a plot of the logarithm of the current density in milliamperes per square centimeters as a function of the cell voltage. And we are looking at 2 mil cathodes with the standard electrolyte which is a 1 1/2 molar lithium aluminum tetrachloride solution in thionyl chloride. LiAlCl_4 .

We have data representing three temperatures: 25, 45, and 65 degrees. What this graph shows us is that over the entire range of current densities here, by increasing the cell temperature, the operating temperature, we realize very substantial improvements in operating voltage.

(Figure 2-43)

This next slide contains some complementary data. We are interested in the discharge capacity as a function of temperature as well, so we are plotting again on the same axis; logarithm, current density, milliamperes per square centimeter.

Now, as a function of the discharge capacity in milliamperes per hour per square centimeter. Each point here corresponds to a point in the preceding slide.

I should mention that all of this data was obtained. Each point was obtained by averaging over the discharge plateau of a separate lithium thionyl chloride cell. So, we are not looking at initial data, we are looking at data that is characteristic of the average performance of the cell.

Again, we have data for 25, 45, and 65 degrees. These curves show that again increasing the operating temperature, and we gain very substantially in discharge capacity, effectively doubling the capacity here at rates of about 20 milliamperes per square centimeter.

(Figure 2-44)

The next slide contains two typical discharge curves plotting the cell voltage as a function of the discharge time in seconds of 2 mil cathodes, again with the standard electrolyte at a rate of 100 milliamperes per square centimeter.

We have data for 25 degrees and for 65 degrees, showing the range of temperatures we covered, and I think this clearly points out the improvement in voltage and the capacity with increasing temperature.

I am going to turn now to the second of the four parameters I mentioned initially, and that is the electrolyte composition.

The standard composition, of course, as I mentioned, is the 1.5 to 1.8 molar lithium aluminum tetrachloride. We found, however, that by modifying the electrolyte by using excess amounts of aluminum chloride from one of the electrolyte constituents, we can greatly improve the high rate performance of the cell. The next slide demonstrates this.

(Figure 2-45)

We are back to polarization curves again. Logarithm current density versus cell voltage. I have data here for two electrolytes and for two temperatures covering the range of temperatures we looked at. There is the data here for the standard electrolyte at room temperature, 65 degrees, and with the excess aluminum chloride electrolyte at room temperature, 65 degrees.

I should mention the optimum performance that we found to be obtained with an electrolyte containing 4-1/2 molar aluminum chloride and thionyl chloride.

This graph shows again over the entire range of current densities and over the entire temperature range. We gained substantially in cell voltage by the use of electrolytes containing excess aluminum chloride. This seems to be true, especially true at the higher temperatures.

(Figure 2-46)

This figure contains the corresponding discharge capacity data. Again, these points correspond to the ones in the preceding slide where we are plotting the logarithm of the current density. And, now, as a function of discharge capacity, milliamperes per hour per square centimeter.

Here is the data for the standard electrolyte at room temperature, 65 degrees, and for the 4-1/2 molar aluminum chloride electrolyte at room temperature, 65 degrees.

This graph shows that not only does the use of the excess aluminum chloride electrolyte improve operating voltage, we also see very great improvement in discharge capacity resulting from the use of the excess aluminum chloride electrolyte.

(Figure 2-47)

This figure again shows two typical discharge curves plotting cell voltage as a function of time in seconds at a temperature 65 degrees and a rate of 100 milliamperes per square centimeter, fairly high rate for this cell.

We have data here for the standard 1-1/2 molar lithium aluminum tetrachloride electrolyte and for the 4-1/2 molar aluminum chloride electrolyte. Again this graph is meant to show in a practical sense here, the improvement in average voltage and the improvement in capacity associated with this parameter.

You can notice more or less this characteristic – in the beginning of the discharge curve, associated with the excess aluminum chloride. This results from the way in which the aluminum chloride interacts with one of the discharge products. And this is shown in the figure which contains the two overall reactions that occur with the two electrolytes.

(Figure 2-48)

In the case of the standard aluminum chloride electrolyte with the aluminum tetrachloride electrolytes, the lithium thionyl chloride produced sulfur and sulfur dioxide which are soluble in the electrolyte, and lithium chloride which is insoluble and which precipitates within the porous cathode.

It is the precipitation of this product within the porous cathode which is responsible for the eventual termination of the discharge reaction.

However, in the presence of the excess aluminum chloride here, aluminum chloride reacts with this product producing the soluble lithium aluminum tetrachloride and prolongs the discharge. In practice, it is the extent to which we can supply excess aluminum chloride to the cell, to the cathode which determines the discharge duration.

Now I want to turn and focus upon the cathode of the lithium thionyl chloride cell, and wonder what we can do to it to improve the high rate performance of the cell.

I listed two parameters originally: the cathode design and the cathode composition. First, we are going to talk about the design. Due to the time limitation, I am only going to talk about the simplest of design parameters. That is the cathode thickness.

(Figure 2-49)

In this figure are shown two polarization curves. Again, we are looking at log current density versus cell voltage, 25 degrees, which is standard electrolyte. The cathode thicknesses range from 2 mils to 50 mils, so we have a fairly large variation in cathode thickness.

You can see that the effect of the increased cathode thickness is not overwhelming, but it is certainly significant. It is also understandable since the electrode reduction of the thionyl chloride has occurred within the porous cathode.

So, as we increase the cathode thickness, we are increasing the internal surface area at constant geometric current density. We are therefore decreasing the specific rate of electrode reduction of thionyl chloride. So we are reducing the polarization.

(Figure 2-50)

This figure shows the effect of cathode thickness variation upon cathode utilization efficiency. Here I am plotting the cathode thickness as a function of the discharge capacity. This comes out to a unit of volume, so we are looking at cathode capacity for unit volume of cathode. This can be thought of as a method of efficiency of the cathode utilization. Again, we are at 25 degrees and at 30 milliamperes per square centimeter with the standard electrolyte.

As we decrease the cathode thickness, the efficiency of cathode utilization gradually increases until, for cathodes thinner than about 6 or 7 mils we get a more rapid increase in cathode utilization efficiency.

Why is this happening? This results because the higher the current density at which the solids discharge, the more the lithium chloride product tends to be deposited toward the side of the cathode which faces the anode.

As the lithium chloride is deposited at the entrances to the cathode pores, the interior of the cathode then becomes unavailable to support further thionyl chloride electrode reduction. So, in practice, the cathode, the higher the discharge rate, the less efficient will be the utilization of the cathode overall. Now, finally, I turn to the last of the four parameters, that of the cathode composition. The standard lithium thionyl chloride cathode is composed of a mixture of carbon black and teflon as in the case of the sulfur dioxide battery. The ratio of the materials, of course, can be varied within a considerable range. There are a great number of different carbon blacks which might be used as cathode constituents.

Of course, a great many other materials and elements are listed in the table as compounds which could be used possibly to advantage as cathode constituents. We examined a number of these, and some of the results are shown in the next figure.

(Figure 2-51)

Here I am back to the polarization curve where I am plotting the logarithm of the current density as a constant of cell voltage at room temperature, with fairly thick cathode standard electrolyte. We are looking at two different cathode compositions.

One cathode contains carbon black and teflon, and the other cathode contains an alternative cathode material. What it shows is that we can gain between 200 and 300 millivolts in operating voltage by the simple replacement of one cathode material, carbon black, with another.

(Figure 2-52)

This figure shows the corresponding discharge capacity data, the log current density as a function of discharge capacity in milliamperes per hour per square centimeter at room temperature with a 2-mil cathode standard electrolyte. The figure also shows the data for the standard and alternative cathode composition. In addition to improved operating voltage, improved cathode utilization can also result from the use of alternative cathode materials.

DISCUSSION

BENNETT: Does the alternate cathode material also give the same type of improvement performance at higher temperatures as evidenced by the original cathode which you used?

KLINEDINST: Yes, it does.

BARNARD: As a possible user of lithium batteries, I would be more concerned with the degradation at the lower temperature, not improvement at the higher temperature. That is a pretty big degradation, really, at the lower temperature.

Do you get the same corresponding degradation in the SO₂ system?

KLINEDINST: I am not an expert on the SO₂ system. I think that question would probably be more properly addressed to someone in the audience who is. I am sure there are many of them here.

TAYLOR: The answer is, no. I think it is generally agreed that the low temperature capability of the SO₂ system is the best of the lithium systems to date.

VASANTH: I am interested in how far the concentration of the aluminum chloride affects the improvement of the operating conditions. Is there a limiting concentration, or do you feel it is indefinite?

KLINEDINST: The four and a half molar is the maximum that is the concentration at which the capacity optimizes and maximizes quite sharply at that concentration. You can certainly increase the concentration further. It decreases the performance.

VASANTH: My second question is, after the improvement of the operating conditions, was the solution analyzed, and was there any component operation taking place?

KLINEDINST: In general, we haven't analyzed the electrolytes.

GROSS: The addition of the aluminum chloride caused some apparent voltage delay caused by voltage overshoot. Can you explain the mechanisms that are involved in this?

KLINEDINST: Yes. Well, in the first place, there was not a voltage delay. What you were seeing was an experiment in which the electrolyte simply contained aluminum chloride. There wasn't any lithium chloride in there at all. This is a reserve-type cell in which the electrolyte is added, and then very soon the discharge is begun.

Well, if electrolyte does not have any lithium on it, then its conductivity is going to be pretty low and you will see a dip in the voltage as the electrolyte is added and the discharge is begun.

So, to answer the first part of your question: The way to get around that is to simply add a little bit of lithium chloride to the electrolyte so that the electrolyte will contain lithium tetrachloride. The reason that happens if you have pure aluminum chloride, the aluminum chloride reacts with the lithium chloride film that is on the anode and that very rapidly produces lithium tetrachloride, which is the conductive electrode salt.

Now, there is first an increase in voltage, and then it drops down. The higher voltage at first is due to really a different overall reaction. In other words, as the aluminum chloride reacts with the lithium chloride, that is as it is produced, you are not forming solid lithium chloride. So the overall reaction is different.

Then, as the aluminum chloride concentration diminishes, you start to precipitate lithium chloride and that is what causes the subsequent drop in voltage.

CLOYD: It looks very good that the actual electrolyte does include the rate capability. In certain applications, however, there is a requirement of the intermittent stop of the current flow.

What is the wetstand capability of that lithium system in the electrolyte like that? Obviously, it gives off protons. Is it at a very fast rate, or what?

KLINEDINST: Of course, it would be temperature dependent. But, I would say that the use of an electrolyte like that would pretty much be limited to a reserve battery configuration in which you do not have long periods of open circuit stand, or low rate discharge involved. The reaction of the aluminum chloride with the lithium anode would prohibit long periods of stand.

Li / SOCL₂ CELL DESIGN PARAMETERS

- **ELECTROLYTE COMPOSITION**
- **OPERATING TEMPERATURE**
- **CATHODE DESIGN**
- **CATHODE COMPOSITION**

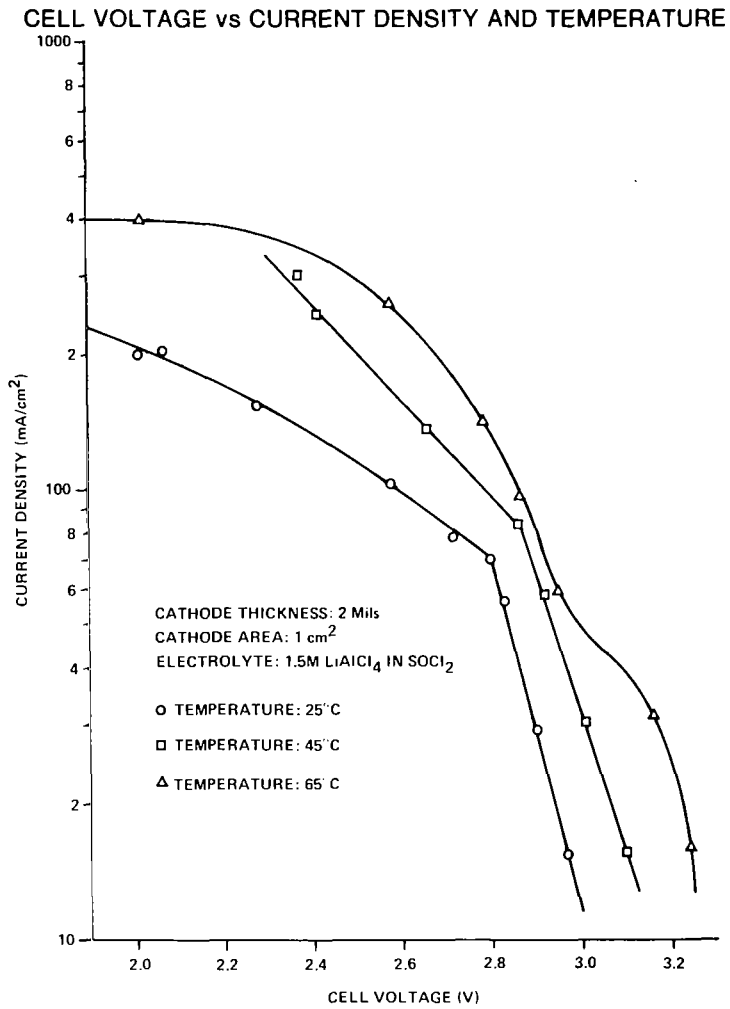


Figure 2-42

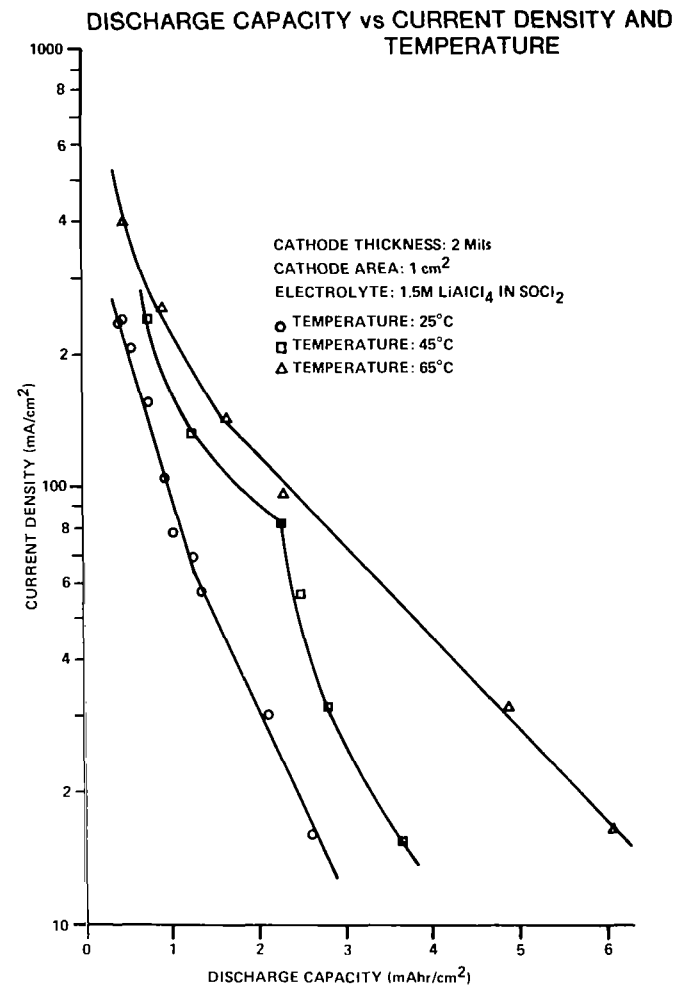


Figure 2-43

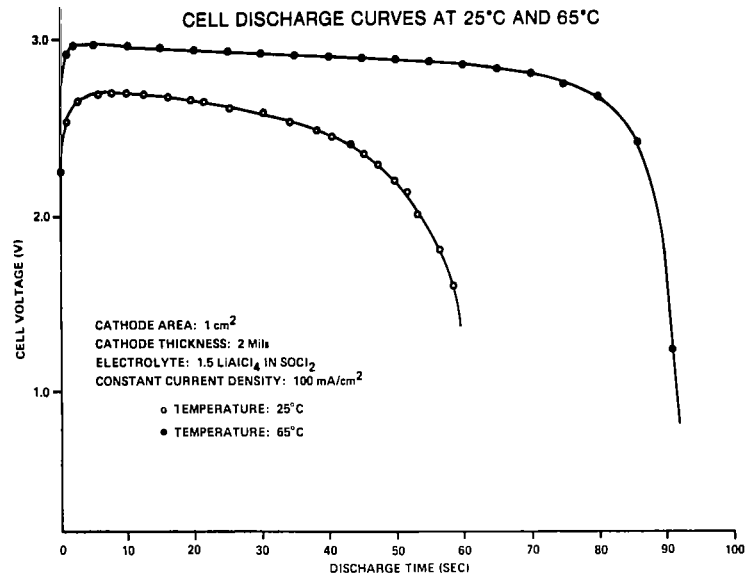


Figure 2-44

**CELL VOLTAGE vs CURRENT DENSITY AND TEMPERATURE
 USING 1.5 M LiAlCl_4 AND 4.5 M AlCl_3 IN SOCl_2 AS
 ELECTROLYTE SOLUTIONS**

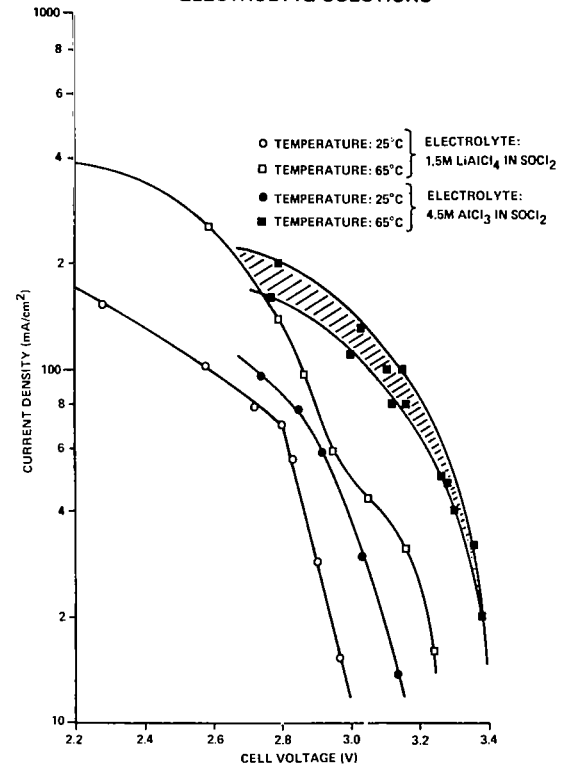


Figure 2-45

DISCHARGE CAPACITY vs CURRENT DENSITY AND TEMPERATURE USING 1.5M LiAlCl₄ AND 4.5M AlCl₃ IN SOCl₂ AS ELECTROLYTE SOLUTIONS

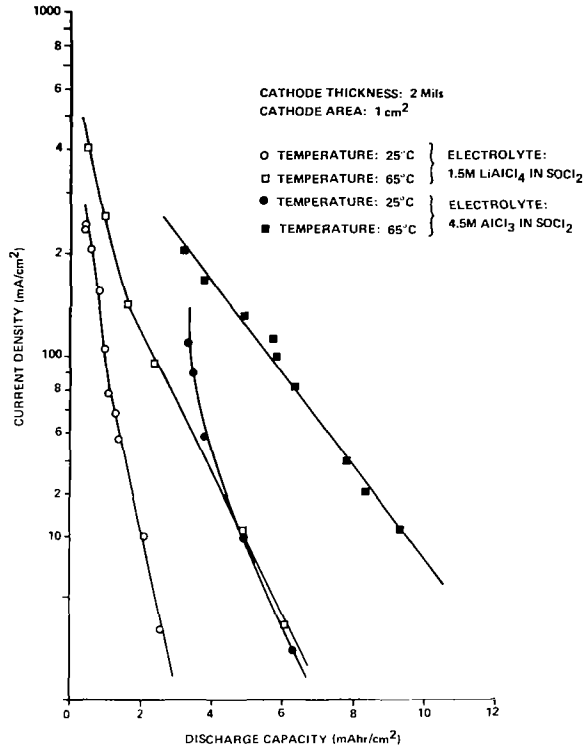


Figure 2-46

CELL DISCHARGE CURVES AT 65°C USING 1.5M LiAlCl₄ AND 4.5M AlCl₃ IN SOCl₂ AS ELECTROLYTE SOLUTIONS

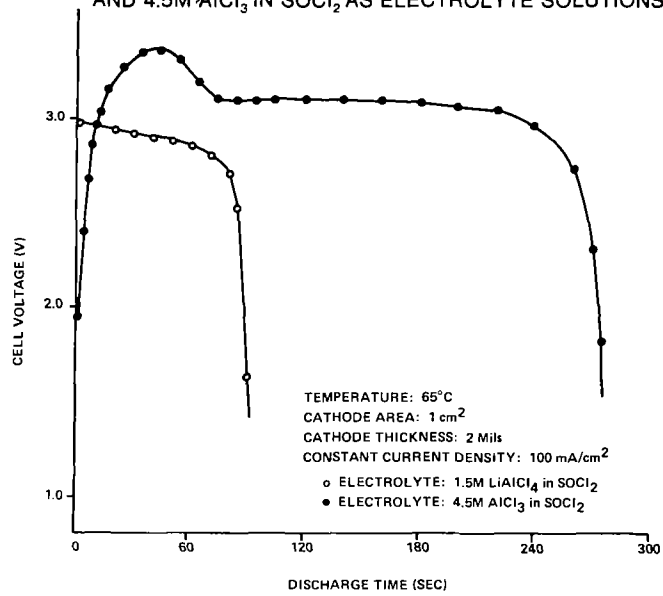
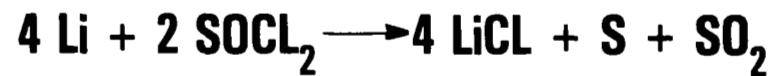


Figure 2-47

Li / SOCL₂ CELL DISCHARGE REACTIONS

WITH LiALCL₄ ELECTROLYTE



WITH ALCL₃ ELECTROLYTE

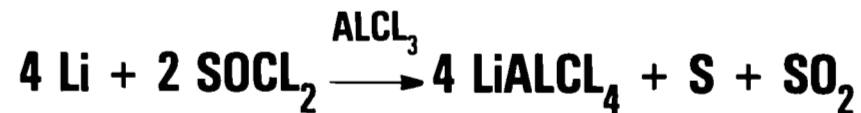


Figure 2-48

CELL VOLTAGE vs CURRENT DENSITY AND CATHODE THICKNESS

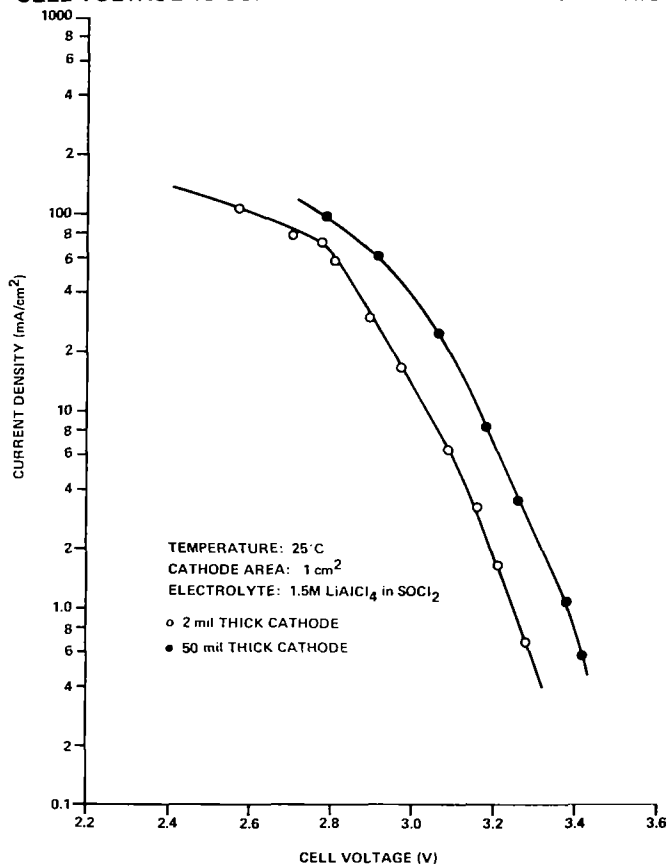


Figure 2-49

CATHODE UTILIZATION vs CATHODE THICKNESS

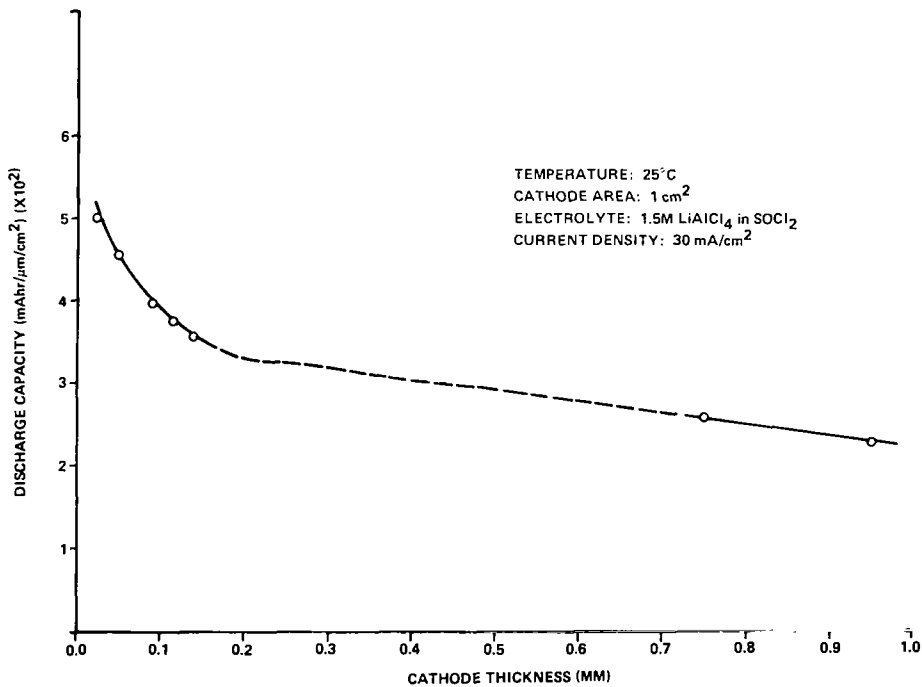


Figure 2-50

CELL VOLTAGE vs CURRENT DENSITY WITH STANDARD AND ALTERNATIVE CATHODE MATERIALS

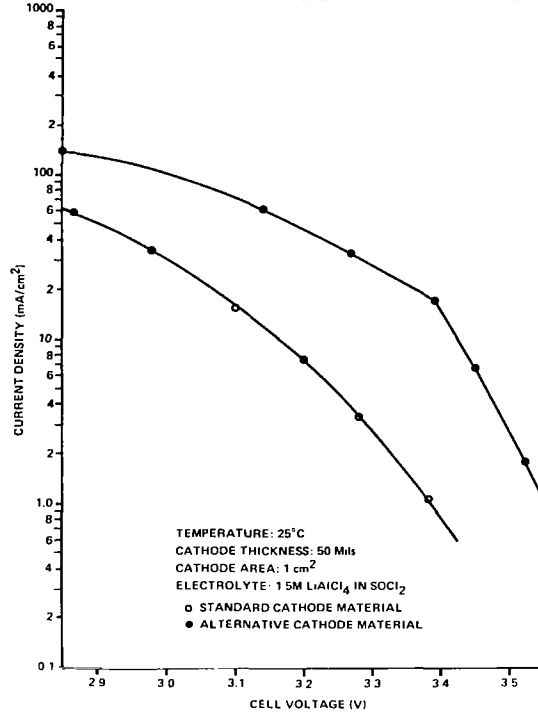


Figure 2-51

DISCHARGE CAPACITY vs CURRENT DENSITY WITH STANDARD AND ALTERNATIVE CATHODE MATERIALS

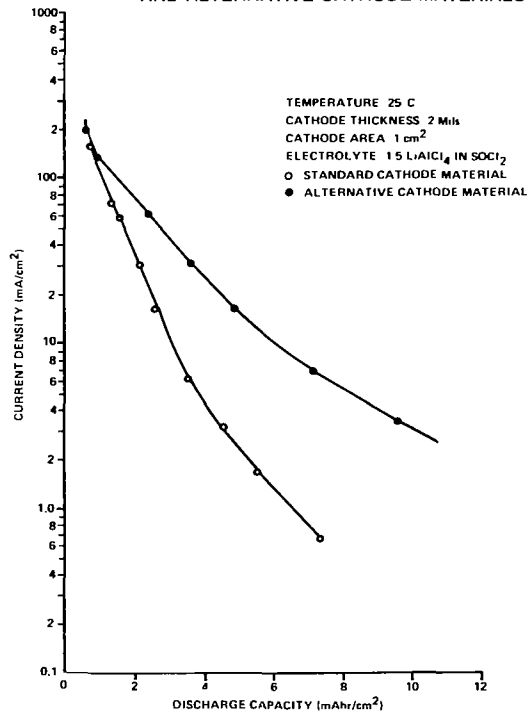


Figure 2-52