SULFUR STUDIES ON LITHIUM SULFUR DIOXIDE BATTERIES

A. Dey
Mallory

Lithium SO_2 batteries are being manufactured in substantial numbers now by various companies and have been sold for several years now.

So there are a lot of users who use these batteries in various ways and try to extract as much as possible in terms of energy. Of course, when one does that, he occasionally runs into various problems. That is a subject that we studied for the last year or so.

The work started initially after we hired Thrombani of NASA. He was trying to use SO_2 D-size batteries at -30 degrees on 2-ampere force discharge, and he found some of the cells caught fire, and so forth, under these kinds of conditions. It was forced-discharge problem that occurred.

Well, when we started to study the problem, we decided that we wanted to look at it as comprehensively as possible, look at the chemistry of the system, try to learn more about the chemistry, and solve chemically as well as by other engineering means. So I will start with some of the work that we have done using DTA off lithium SO_2 battery chemicals.

(Figure 2-22)

The first figure shows DTA of lithium and SO_2 by themselves. Lithium is the anode active material, and SO_2 is the dipolarizer. Of course, we want to know how stable they are.

As you see, this is the heating curve here. This endotherm corresponds to melting of the lithium, and then we continue the heating to 320 degrees. In some experiments, we have increased that to 350 degrees. As you note, there is no exothermic reaction between the two very reactive materials. These are the materials which give you the energy of the battery.

This is a cooling curve where you see again that the lithium is freezing off, and again there is no reaction. That demonstrates the protective nature of the film which is the product of these two product of the cell reaction which is lithium dithermonate, a solid crystalline material which coats the lithium as soon as these two are mixed. That coating is sufficiently stable so that even under such extreme conditions of heating, nothing happens. So lithium and SO_2 is very stable.

Next, we did the DTA of lithium and acetonitrile which is the organic solvent compound of the electrolyte. The DTA is shown in the next figure.

(Figure 2-23)

The figure shows the lithium and acetonitrile. As you see, it is very, very reactive, and it reacts even at room temperature. In fact, here, the initiating temperature is roughly 58 degrees. If you have very little lithium, you may see them react with heat evolution even at room temperature. Of course, the amount of heat generated is quite significant to cause hazard.

So, these are the two components the most responsible for all the behavior, all the unsafe behavior that we heard and we saw ourselves.

One of the things I think I should point out is that exotherms initiate at a certain temperature when you heat it up. That is the good parameter which determines the stability of the system. So, we use that parameter to develop alternative electrolytes. The lower the temperature of this exotherm initiation of this reactive reaction, the more unsafe the situation is. We would like this to occur at the highest temperature possible in an actual cell.

In the next figure, we show the DTA of the lithium, and the electrolyte.

(Figure 2-24)

The electrolyte consists of acetonitrile, SO_2, and lithium bromide, 70 percent of SO_2.

You notice again the heating, the initiation of the exotherm occurs at 170 degrees. It has been increased from 50 degrees or so, which you saw in lithium acetonitrile to 170 degrees.

This exotherm is due to the lithium and the acetonitrile. Just as in the presence of SO_2 that temperature is increased, so the lithium SO_2 battery will be able to sustain this kind of temperature, but no more. If you go beyond that, you will have a problem.

We have looked into the possibility of developing alternate electrolytes into which the exotherm initiation temperature is going to be. So, it is actually higher than what we find with lithium acetonitrile by themselves. You have noticed that the SO_2 electrolyte contains SO_2. The presence of SO_2 itself has done a tremendous improvement, 70 percent SO_2.

We are interested in finding out what is the lowest concentration of SO_2 needed for lithium acetonitrile reaction to be suppressed. That we did by measuring the exotherm initiation temperatures of the lithium acetonitrile, those two complements, as a function of SO_2 concentration. That is shown in the next figure.

(Figure 2-25)

Here are the exotherm initiation temperatures in degrees Centigrade. These are temperatures at which the exothermic reaction begins between lithium and acetonitrile. And we are adding SO_2 in that solution. Here is the percentage of SO_2. When there is no SO_2, the exotherm is initiated as you see, roughly 50 degrees, or thereabouts, a very unsafe situation.

So, if you have a cell where all the SO_2 is consumed, obviously you can expect that cell to behave in an unsafe manner because of the lithium energy problem. But, as you add SO_2, note that even at high percent SO_2 in the cell gives you quite a bit of protection. The cell can stand quite high temperatures before it can generate exothermic heat, causing all kinds of problems.

Of course, we have completed the experiments of in transial moisture. As you see, these points, adding 1 percent moisture. It does not seem to make that much difference between addition of 1-percent moisture and no addition at all, because moisture there also has some protective action. At least it does not have a deleterious action in that sense in these kinds of concentrations.

We did the experiments with lithium powders, and there you see you need quite a bit, almost 25 percent or so, to get protection. Lithium powder, of course, will have a very high surface area, and there, if you do not have sufficient amount of SO_2, you may see exothermic initiation at an earlier stage.

So these studies tell us that one must have design cells so that during their use and abuse there should be sufficient SO_2, at least 10 percent or so present in the cell which will protect the lithium that is left over, or lithium powder, or any other lithium products generated during the cell use and abuse.

(Figure 2-26)

Now this figure shows similar kinds of data. Instead of SO_2, we have used a second organic solvent with acetonitrile, so again we show the exotherm initiation temperature as a function of concentration of a second organic solving, which is very protective. Probably carbonate is in one instance, and acetic hydride in another. Both of these solvents, when added to acetonitrile, provide protection to lithium as evidenced by the increase in exothermic initiation temperatures. These are the temperatures at which lithium acetonitrile will react exothermically.

Again, you notice the 5 percent, or 5 to 10 percent, of this second solvent is sufficient to give protection to lithium, and hence potentially can provide the same for a cell.

We have tested a whole variety of organic solvents as additives and developed six different organic electrolytes which have conductivities similar to the conductivity of the standard electrolyte containing acetonitrile and lithium bromide.

Of these six, I believe two of them did not have any acetonitrile at all. Since the conductivities are very comparable, we have good reason to believe the performance of these cells probably will also be comparable.

We are now in the process of testing these in actual cells for storage and for performance at low temperature as well as for safety, and I hope that we shall be able to report on that soon.

Now one can look at the lithium SO_2 battery as a whole as if it were an alternative system. It has three basic reactive components: lithium, SO_2, and acetonitrile. So, from design of safe cell,

one can then look into this alternative diagram and can come up with certain approaches to make safer batteries.

(Figure 2-27)

In this figure we show an alternative phased diagram to explain this. We have the SO_2 here, lithium here, and acetonitrile here. So, in a battery when it is made, the composition of these three materials will fall along these lines when the battery is made. These are all the possible stoichiometric conditions that you can think of that will fall in this line.

Now one can, by design, make the batteries so that the composition falls somewhere around here. If it is somewhere around here to begin with, when you discharge the battery, one consumes both SO_2 and lithium in a very, very predictable manner based on SO_2.

Now, that has been established very well. The reaction is also very efficient, 100 percent efficient. As you discharge the cell, the composition inside the cell of these three materials changes in a manner such as this. Therefore, at the end of the discharge, you end up somewhere around here.

Now, when you end up here, this is a condition in which you do not have any lithium left. All the lithium is gone. You have plenty of SO_2 left, and you have plenty of acetonitrile. This is then a lithium-limited design, as you have heard mentioned earlier, a design according to what we have talked about, a safer situation.

On the other hand, if you are here, then as we discharge the cell, you move in this direction, you end up with a situation where you do have some lithium left, and you may or may not have SO_2 left, depending on where you are. In fact, here you have no SO_2 left, and therefore you would expect the unsafe behavior ensuing because of the action between lithium and acetonitrile, as we have been illustrating.

So this is then a design which has excess lithium. This, of course, assumes that the efficiency of discharge of SO_2 is 100 percent.

Now, as you know, SO_2 is discharged at carbon cathodes. Depending on the activity of the carbon cathodes, you may or will not use all of the SO_2. The efficiency of utilization of SO_2 may vary depending on the quality of the cathode or the amount of carbon in the cathode and so forth. So, that is another parameter that one has to consider for a safe design of SO_2 battery.

Now, from all of this we can say that we do know quite a bit about the system. It is highly predictable because of what we have found, and therefore we can design the cell to take all kinds of abuse and use conditions.

To give you just two examples of the forced discharge that I mentioned in the beginning.

(Figure 2-28)

In this figure, I show in voltage and temperature profile, a D cell which is forced discharge at -30 degrees at 2 amperes.

This is a cell which contains excess lithium by design. You will notice here, this is the voltage, that is the temperature, and this is the number of hours, at -30 degrees at 2 amperes.

Notice initially you have a cell voltage of up to 1 volt. There is gradually a decrease and reaches zero volts. Now, if you had a reference electrode in this cell, you would find the cathode, the carbon cathode. These voltages are characteristics of the carbon cathode only. Lithium voltage remains constant. Lithium potential remains constant. It is the cathode which goes through this.

So, we know that above zero volt, all you are having here is basically reduction of SO_2 primarily. Then, you reach 0 volt. Below zero volt, what you have here is also quite predictable. You are having deposition of lithium on your carbon cathode and on your aluminum exotherm.

Dr. Taylor in our lab demonstrated that, in fact, what you have is a lithium-aluminum alloy formation on the cathode in this area when the cell voltage is negative.

Also, notice that during this place when the cell is polarizing, of course, you are generating the energy that is not delivered, utilized in generative heat. So, you heat up the cell during the polarization phase. But, beyond zero volt, basically what you have is the deposition of lithium on your carbon cathode aluminum grid and dissolation of lithium on the anode, two reactions very reversible. Therefore, you have cooling basically, because you don't generate any heat. So, you are piling up a lot of this lithium-aluminum alloy and lithium dendroids during this phase.

Then, you reach a point, a very sharp reversal, and this is due to the fact that you have consumed all the lithium on the anode. There is no more lithium left; therefore, you polarize yourself severely, and that is the time when there is sufficient heat to cause this lithium material to get fired. We have a very rapid temperature buildup, temperature rise. Of course, this is the time when you have cell venting, sometimes violent venting and sometimes even fire.

So, because of all this activity when the cell is below zero volt, this occurs because of the excess lithium.

Now, if you design a cell so that the amount of lithium, the polarization of the lithium electrode is going to occur here instead of here, you just reduce the amount of lithium on your anode, and you make the cell go through this deep reversal at this point right here.

When that happens, there is not enough active lithium present to give you any problem. All you can see is venting or not venting at all.

We have tested many, many D cells with the lithium-limited designs at 2 amperes and -30 degrees and demonstrated this to be the case.

The next figure shows a typical voltage profile of such a balance, but a lithium limited cell. Assumption again is the same cathode in both cases.

(Figure 2-29)

Here is the voltage profile. You have about 2 volts for a while, and then it gradually declines. You see the voltage goes to deep reversal right at the point when the cell sees 0 volt. There is no chance for the formation of this active material I mentioned. You see that cells keep up at this point, and during the deep reversal you are wasting a lot of energy. That energy must show up somewhere. It is showing up, but it is not sufficient to give you any problem.

The cell either vents and, in fact, in most instances there is no venting at all. So, then by design, one can make these cells undergo all kinds of abuse, including very severe discharge, without any problem.

Another thing you must remember is that this characteristic, the number of hours that the cell is going to give you above 2 volts under a specific load, depends on the carbon cathode, a very important parameter. That is an area again where we have a tremendous improvement, although the cells do not vent at all.

A third possibility, also, perhaps I should mention, is that -- although I mentioned about the lithium-limited design and that, of course, has advantage not only from the forced discharge standpoint, but also from the point of view of disposal -- to establish that if you have lithium-limited design, you do not have formation of cyanide, and so forth, which certainly is an advantage.

(Figure 2-30)

But I must emphasize that all of these are dependent on current density of the total current. A cell, which is designed for 2 amperes and which can take that kind of abuse, if you increase the current to 5 or 10 amperes, this, of course will not be true. So the cells have to be designed for a particular current operation.

DISCUSSION

BIS: I was a little bit confused when you did the electrolyte and the lithium, when you conduct the exotherm at about 200°C. Then you went ahead and did lithium, acetonitrile, and SO_2; you showed a curve that got up to about 400°C.

DEY: No, 400 degrees. That is with the lithium SO_2. 400°C, I am sure. It cannot be. Can you show the figure? I think you are talking about the one with the addition of SO_2.

BIS: Right.

DEY: That's figure 2-24.

BIS: Now, you have got roughly 25 percent SO_2 in there, right?

DEY: Yes.

BIS: Now, your electrolyte is 70 percent SO_2, is it not?

DEY: Yes.

BIS: What would your normal electrolyte composition on there be, assuming you eliminate the lithium bromide?

DEY: That was 70 percent. These are separate experiments. It is a good point. We did see some variation in that initiation temperature, depending on the specimens that you used, lithium specimens.

The experiments that we used earlier, we probably had some more active lithium specimens that may not have as much filler to begin with.

BIS: There is no lithium bromide in this, right?

DEY: No. That is a good point, too. Lithium bromide does catalyze some of these reactions, exothermic reactions.

BIS: That could lower the temperature?

DEY: I think that is right.

BIS: My second question is, basically have you done any chemistry, basic chemistry on these cells as a function of discharge rate storage? In other words, identification of species within the cells themselves?

DEY: We have done quite a bit, and we are continuing to do quite a bit of it. We expect to publish some of this soon. It is still in the works.

WATSON: Dr. Dey, in the lithium limited cell, you obviously don't utilize all the lithium at the end of your useful life. You are using the lithium as a current collector, so there is a certain percentage left over.

Do you have any feel for how much lithium is required before you enter the hazardous region?

DEY: If you do not have any current collector at all, then, of course, you have to have a finite amount. Now, what is the exact amount, I don't remember, what is the exact amount in terms of ampere-hour. But, there is a certain amount, and that will depend also on the design; how the electrodes are made, how it is connected, and to what it is connected. Because what

basically happens when you use the lithium up, you may not use it uniformly, depending on your cell design. If you don't use it uniformly, you may cut off a ceratin portion of lithium at a point very near the tab or near the connection. In which case, of course, you end up with a lot of lithium present.

So, care has to be exercised to how you design your anodes, how you connect it, and how uniform the reaction is to the spiral.

WATSON: One other thing. Why does it break near the tab?

DEY: Why? It will break if you don't design the cell properly. You may have reaction near the tab more than further away from it. That is strictly on cell design. This is very important.

ANGRES: I get the impression you tried to get away from acetonitrile.

DEY: Yes. And for obvious reasons, which is that it is a reactive component. It has some beneficial effect in terms of performance, but we are trying to see whether we can, in fact, get away from it or develop an electrolyte which can moderate its reactivity.

ZOLLA: Instead of a mechanism whereby you rely on the design according to the rate to safeguard you against this reverse voltage failure, would you not prefer to see a flat line design as seen in the previous paper whereby it is intended to break, and one does not have to worry about whether, in fact, one is sticking to the original design or just one parameter, one radius?

DEY: What design is that?

ZOLLA: The previous curve you saw shows the reverse voltage, as you entered reverse voltage, a flat line characteristic, which is independent of forced discharge rates.

I was just asking if you would not prefer to see that kind of characteristic in your cells.

DEY: Are you mentioning about the accounting battery where we are talking about?

ZOLLA: I know it is a different cell, but the same possibilities are there.

DEY: I wish that design were discussed in some detail, so I can make an assessment.

ZOLLA: I wish I could tell you all about it.

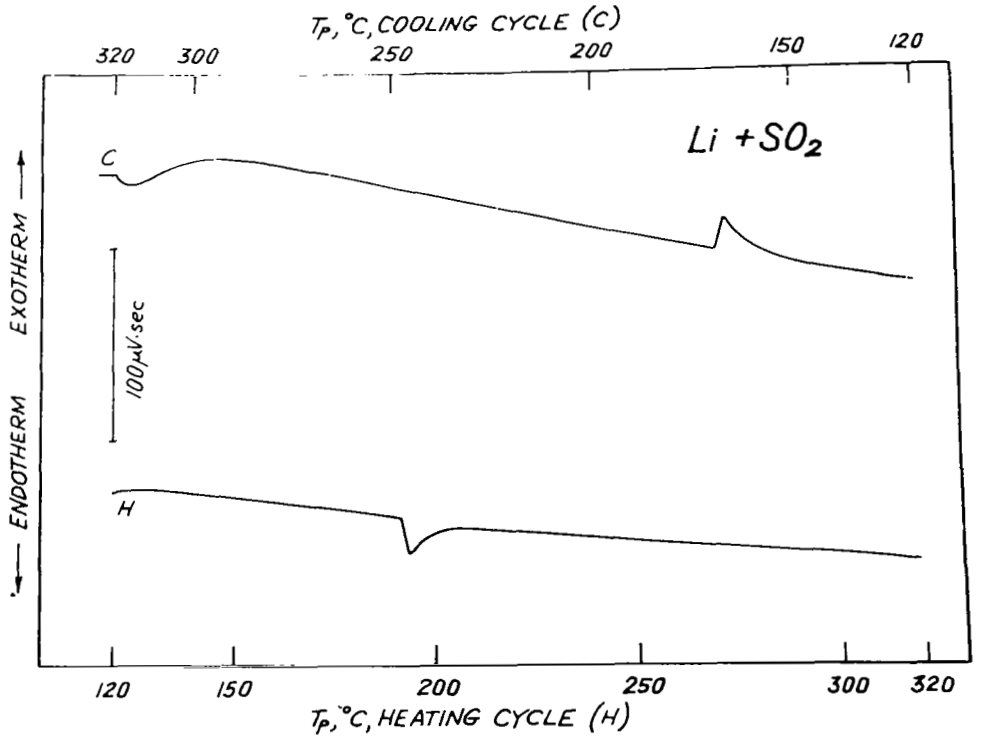


Figure 2-22

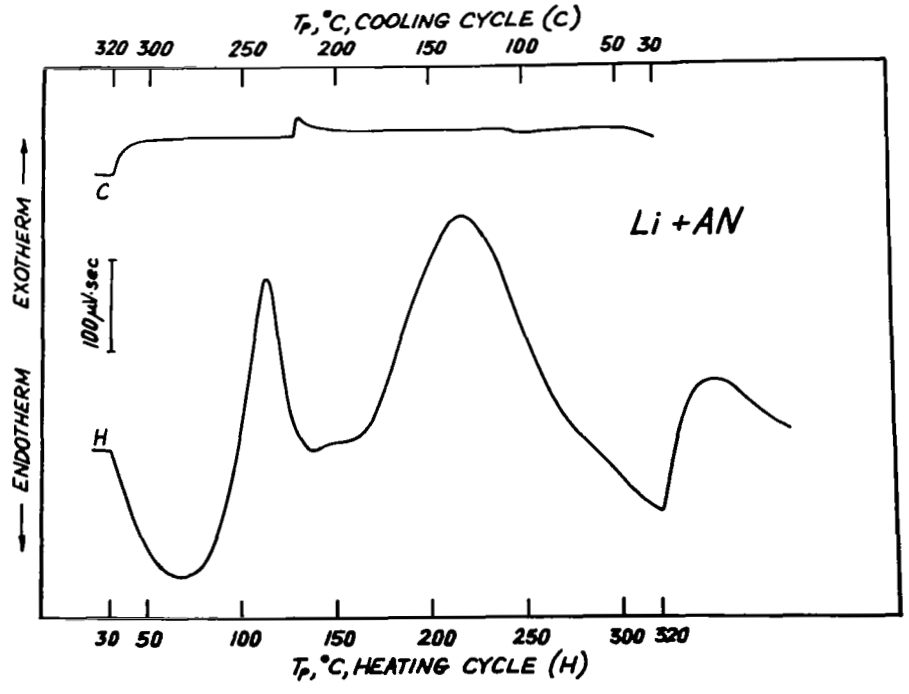


Figure 2-23

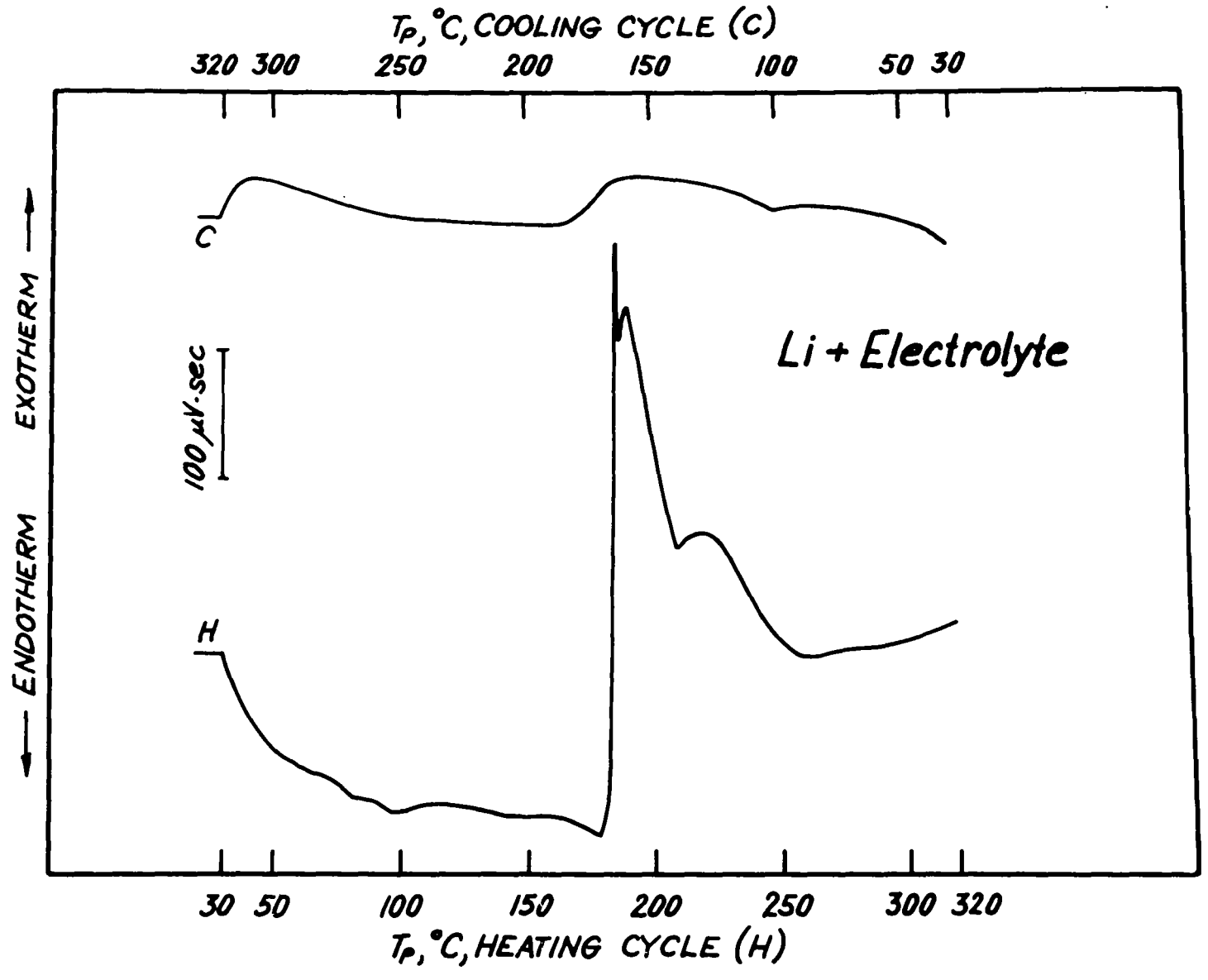

T_p, °C, COOLING CYCLE (C)
320 300 250 200 150 100 50 30
C
EXOTHERM
ENDOTHERM
100 μV·sec
Li + Electrolyte
H
30 50 100 150 200 250 300 320
T_p, °C, HEATING CYCLE (H)

Figure 2-24

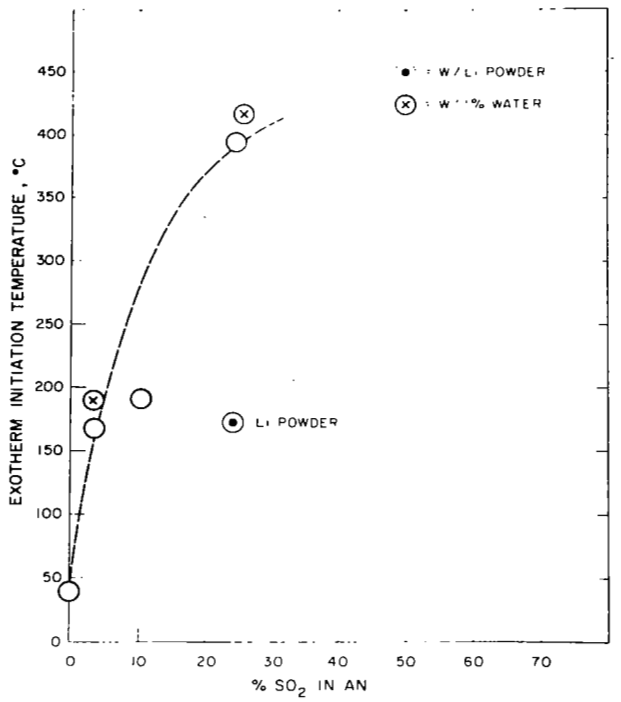


Figure 2-25

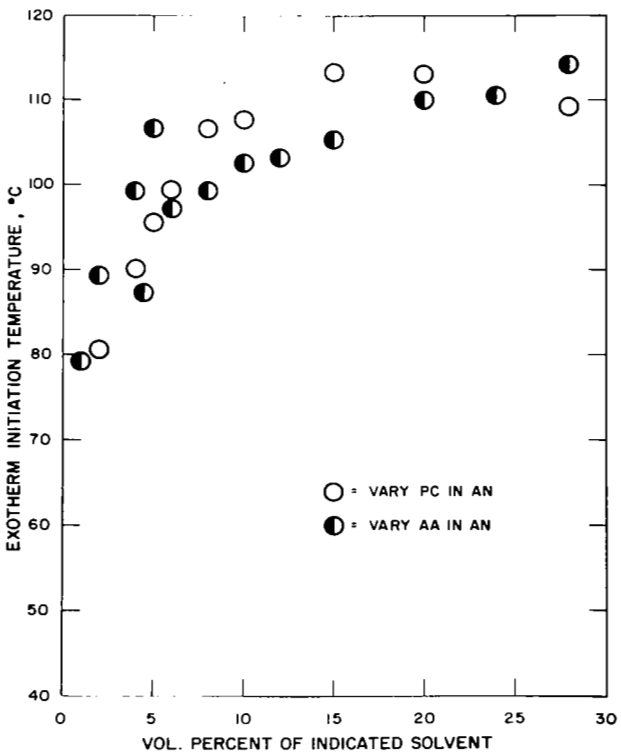


Figure 2-26

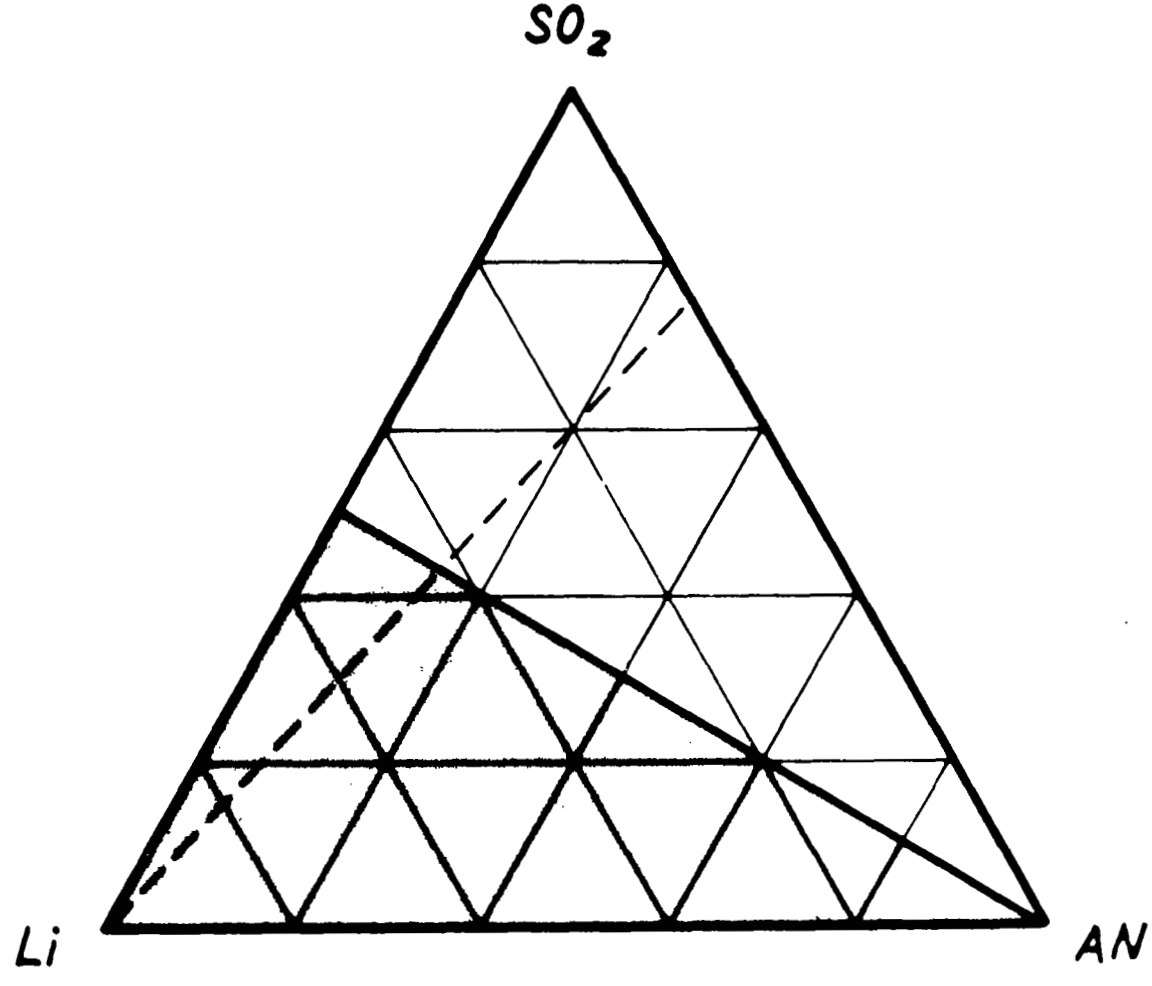
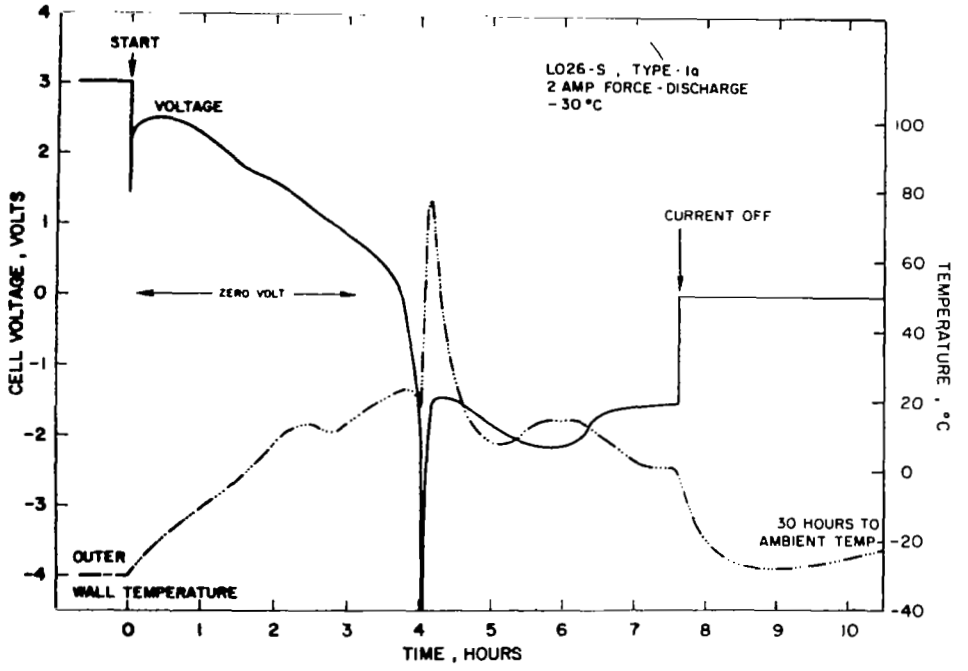


Figure 2-27



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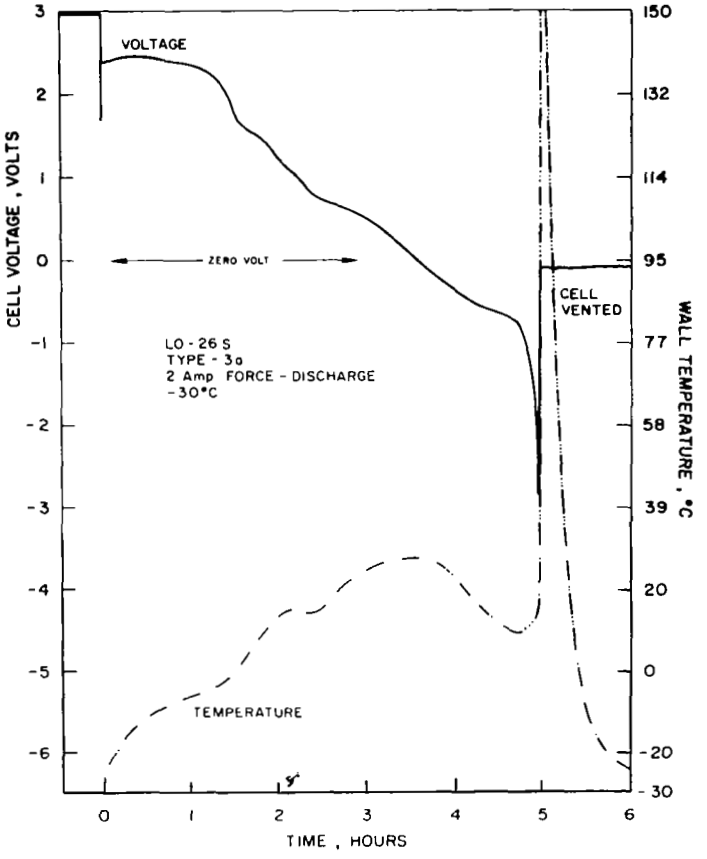

Figure 2-29

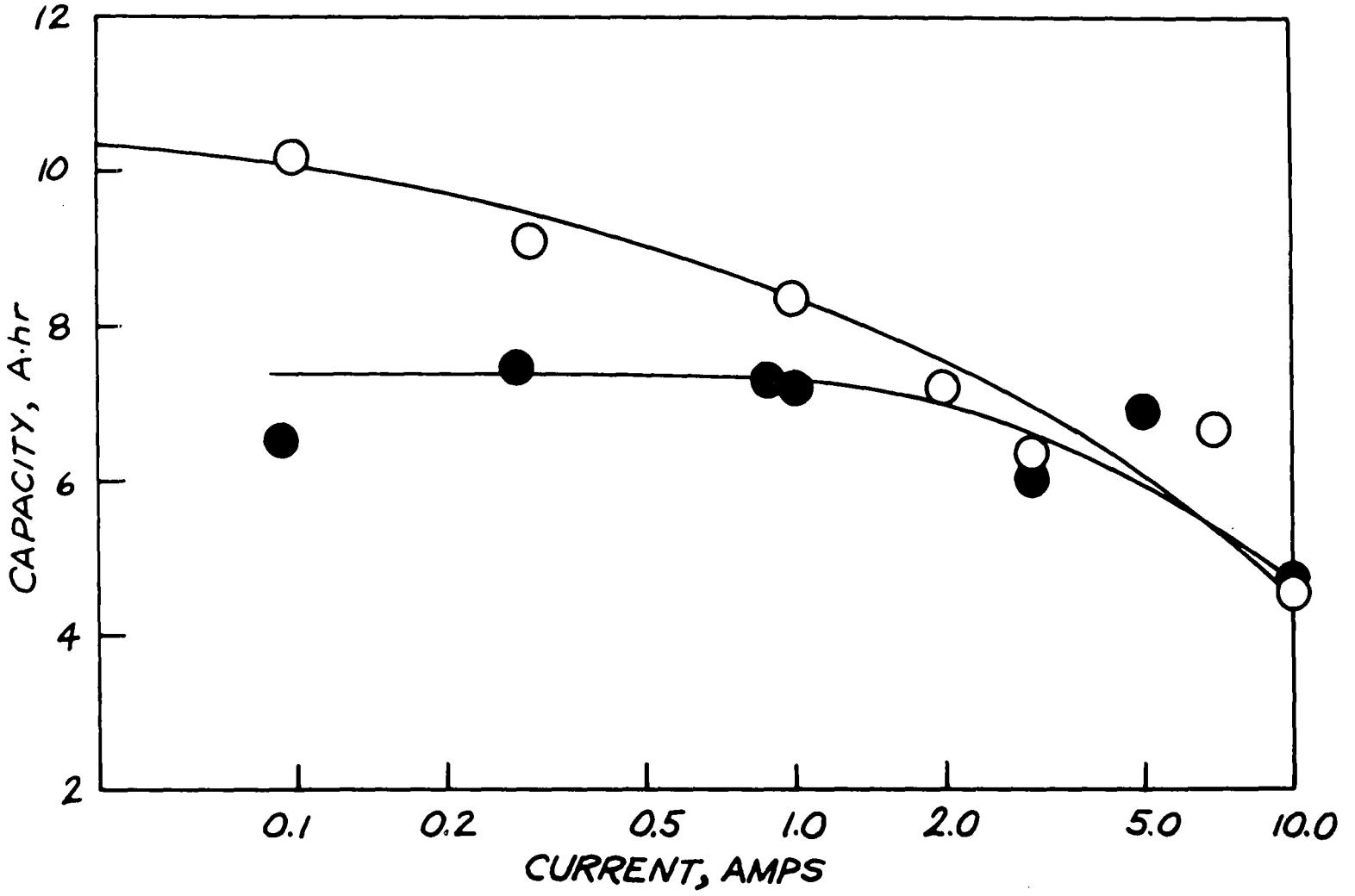

Figure 2-30