HIGH RATE DISCHARGE STUDIES OF LI/SO_2 BATTERIES

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ABSTRACT

A battery composed of twelve lithium/sulfur dioxide "D" size cells in series was forced discharged at 21 amperes. This current was established by the proposed use of the battery and represented a discharge condition which the battery manufacturer felt might produce venting. Discharge of the battery into voltage reversal resulted not only in cells venting but also in the violent rupture of at least one cell.

INTRODUCTION

The Lithium Systems Safety Group at the Naval Surface Weapons Center was recently asked to evaluate a battery under consideration for use in a piece of Navy equipment. The prospective user asked us to determine the battery's voltage response under forced discharge at 21 amperes and to characterize any safety hazards associated with this discharge. The Navy user provided us with several samples of a battery which had been proposed for the equipment by the equipment's manufacturer. This paper briefly describes our tests and some of the more dramatic results which we obtained. The experimental results and the data collected as a part of this evaluation offer several lessons to the community of lithium battery users.

EXPERIMENTAL DESIGN

The sample batteries were first characterized by physical inspection and the measurement of their open circuit voltage and AC impedance. Forced discharges were effected using a DC power supply limited to 21 amperes and 36 volts (the open circuit voltage of the batteries). Battery potential and battery temperature were measured at regular intervals throughout the experiment. The potential drop across a calibrated shunt was used to measure the current actually flowing in the circuit. All discharges were conducted in a facility designed for hazardous testing.

BATTERIES TESTED

All of the sample batteries contained 12 high-rate "D" size lithium/sulfur dioxide cells connected in series. Each battery was fused at 30 amperes with a "slow-blow" fuse. The batteries contained two hexagonal layers of six cells held together one on top of the other with elastic cement and enclosed in outer wrap of plastic film and cardboard.

The batteries were delivered to us by the Navy engineer who was considering them for use in a piece of equipment. He had obtained the batteries from the contractor who was developing the equipment. The contractor had in turn obtained the batteries from a manufacturer who had built the cells and assembled the battery. Upon inspection, it was clear to us that some of the batteries had been used and/or had developed internal problems during the course of this handling. The results reported in this paper represent data obtained on a battery which exhibited no physical or electrical indication of use or deterioration.

In order to obtain as much information as possible about the battery, we asked the manufacturer for information about the battery's history. The available records indicated that the batteries were probably assembled in mid-1979, a time consistant with the data code on the cells which showed that they had been built in April of 1979.

The manufacturer's representative was very helpful to us when we sought this information but was quite surprised to learn that we planned to evaluate batteries which were then four years old. We were told that our results would have only general applicability relative to the behavior of a battery built in 1983 because the construction and performance of the cells had been modified and improved several times since our batteries were built. Upon clarification, we learned that although the cells built in 1983 retained the same description and catalog number used in 1979, the cells actually were different enough that the manufacturer's representative doubted that our test results would apply to a new battery.

POINT 1

The information just summarized is a clear example of this paper's first point for lithium battery users: manufacturers often change cell designs, and these design changes are not always accompanied by a change in catalog number or description. This practice of incorporating changes into a cell without changing the catalog number seems to be the regular procedure of at least several of the major battery manufacturers, it is certainly not limited just to the cell we were testing. The community of users must view this practice with ambivalence. Manufacturers introduce changes into a cell to provide a product which they view as safer, more effective, and/or less expensive. Although users must find these goals to be generally admirable, we cannot help but be concerned that these "improvements" can reduce or destroy the value of performance data obtained on earlier versions of a cell. For data which required substantial time and effort to collect suddenly to become less useful because of a change in cell construction can be a very serious loss. The loss can be even harder to manage if the changed cell retains an unchanged catalog number.

BATTERY DISCHARGE RATE

The use for which this battery was suggested required that it deliver 21 amperes at 28 volts for several minutes over a wide temperature range. This current represents a very demanding, perhaps even abusive, discharge rate for any "D" size lithium/sulfur dioxide cell, even one of "high-rate" design. The battery's manufacturer was concerned enough about the consequences of a discharge at this rate to label each battery, "Caution: This battery when discharged at customer-required rates can be expected to vent SO_2 gas. Use extreme care to avoid breathing toxic fumes." The manufacturer's catalog also cautions against constant discharge of this cell at currents above 1.3 amperes.

POINT 2

The second point of this paper is now clear: users often ask more of a battery than it was designed to provide. The battery manufacturer's literature on this cell suggested that the battery would only marginally meet the discharge requirements of the equipment at room temperature; and at -40°C, the problem would have been even more severe. The contractor designing the equipment still proposed this battery in spite of clear indication that safety or performance problems would probably exist. The prudent user will make an effort to understand the limits of a battery as early as possible during the design process.

RESULTS OF FORCED DISCHARGE

Figure 1 shows the voltage and temperature data obtained during forced discharge of the battery. At a constant discharge current of 21.5 amperes, the battery voltage dropped from an open circuit value of 36 volts to 23 volts. The voltage recovered to about 26 volts before it began to drop as the battery was forced into reversal. About 20 seconds after voltage reversal occurred, one side of the battery was suddenly and noisely engulfed in flame. Subsequent failures (presumably at the cell level) spanned almost two minutes and bathed the battery in flame. Then a sharp, distinct BANG occurred. The battery fragmented, and cells were scattered over a radius of more than eight feet. (At the oral presentation of this paper at the Battery Workshop, a video tape recording of the battery failure was shown at this time.) The cells were collected and examined after the test. It was clear that most of the cell cases remained intact, and that these cells vented through the vents manufactured into them; but at least one case lost its end and another ruptured through its side.

POINT 3

Lithium/sulfur dioxide cells which have been discharged into voltage reversal at high rate can fail with significant violence. The failure described here is more severe than any we have previously observed for similar cells under conditions of abusive discharge or over discharge at room temperature.

SUMMARY

Our specific results are of particular value to the potential user of this specific battery, but we have identified three areas of concern for battery users in general.

- One must be aware that the characteristics of lithium cells may be changed as manufacturing processes are changed.

- One should avoid forcing a cell to perform beyond its safe design limits.

- One should be aware that even lithium/sulfur dioxide cells with vents can fail with a "BANG" when forced into voltage reversal at high rate.

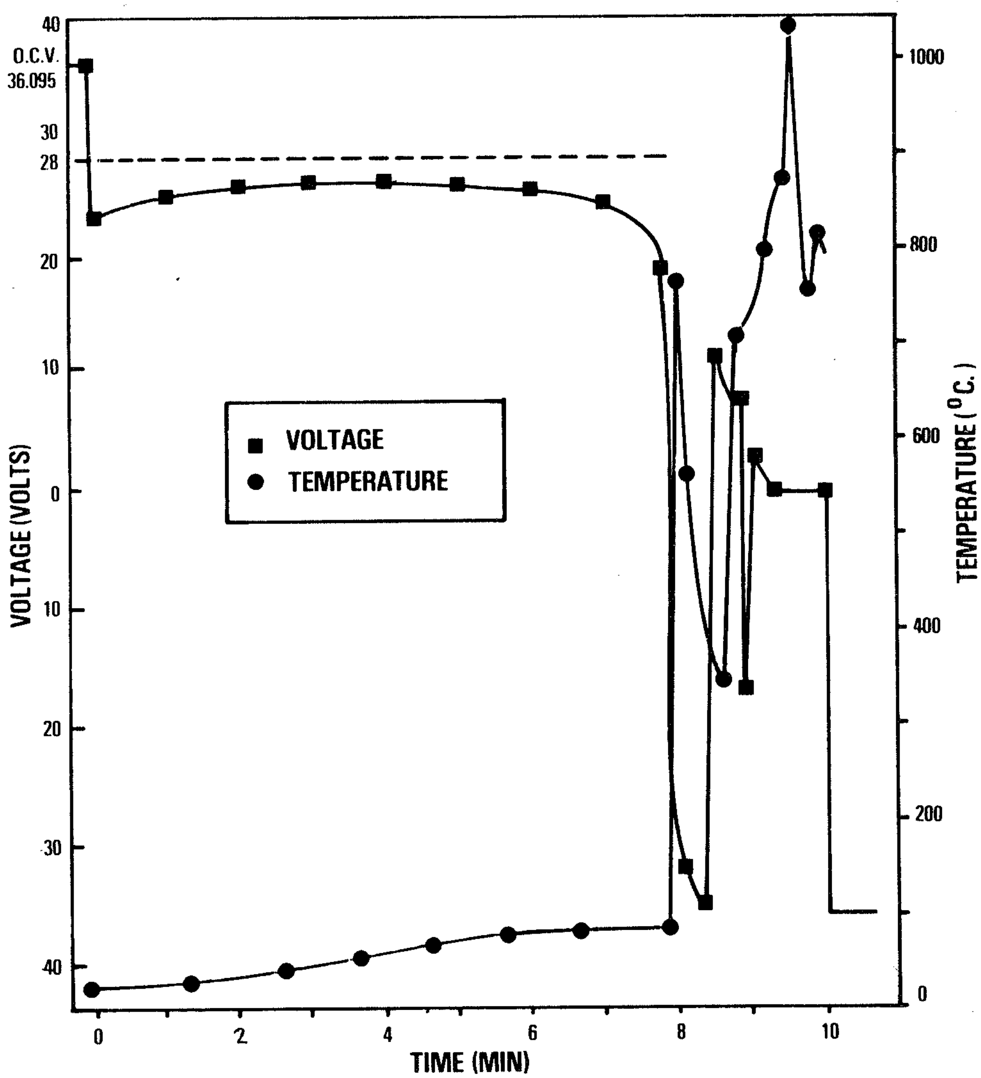

Figure 1. Voltage and temperature data for the forced discharge of a battery at 21 amperes.

Q. Halpert, JPL: This is a panel of experts and rather than having a panel of four or five members up here we have a panel of experts out here in the audience. The business of safety verus non-safety continues to go on. And depending on who is up here speaking and on what system they're speaking about, there's still a question about whether we can build a "safe cell". And it turns out that Gil Roth here from NASA headquarters has been asking this question for a long time - can we build a safe cell. I'm sure he'd like to see that one in NASA applications. But I thought I'd take an informal poll to see how we stand on the issue. Let's restrict it to Lithium SO_2, Lithium Thionylchloride or the BCX system. Is there any one of those systems that - let me phrase the question differently - do you feel we can build a safe cell for any application from those three electrochemical systems? How many of you feel as though they can build that? Is there a safe cell? Ah! There are some people that say I'm opening up the whole world. I want to know any application you could think of that you would select - SO_2, Thionychloride or BCX cell for use and feel - safer and that word has always got to be a defined word. I'm leaving that open now too. I saw some hands.

A. Allvey, Saft America, Inc.: I think you should phrase the question another way. It's basically my contention that there is no battery system - or very few - that I can't make hazardous, so the answer by definition is that you cannot build a safe battery system.

Q. Halpert, JPL: Well I was going to ask that as the second part of my question. I was going to ask you if you could build a safe and if I got no answer I was going to ask is everyone of them hazardous and then we'll go from there. But we do have some people who think that there is one of those three systems, in some applications, that can be safe. I saw four or five hands. Would anyone want to describe a system? Al Willis is using a cell and he raised his hand. Would you be willing to speak to the issue, Al?

A. Willis, Boeing: We have been experiencing the application of the lithium cell to the minuteman silos. GTE has built an assembly of cells or submodular three cells which, in any opinion, is built like the proverbial house and, as such, it has withstood all the abusive testing that we have been able to give to it or, that is, not necessarily me but the military. We have completed the discharge of one set of batteries in the silo satisfactorily and are now in the process installing some others in other silos. Last year I made an investigation concerning what happens when you operate several cells or several batteries in parallel. I speculated that potentially if you had one cell go bad in one battery, you would have a sharing of that current. In other words, would go down and then the other batteries would have to pick up the load. And so you would have a sharing of the load depending

A. Willis, Boeing (Con't): upon the voltage of each of the batteries. And as you got near the end where one cell would go bad in one battery, the other batteries would have to pick up that load until such time there was essentially one bad cell in each battery if you kept it going that length of time. This is a schematic of the installation where there is a power bus. There is a controller between the batteries and the bus. And when the bus got to a certain voltage the batteries were cut in. And the batteries were used until a certain voltage was reached and they were cut out of the circuit. There is nine cells in each battery. There is a diode and a fuse in each battery, as shown. Getting into the area of what happens when one cell goes bad, in this particular application - the OCU of 9 cells at 3.65 is 32.85 volts. The controller had a cut-off of 36.25 volts and so if all the cells went together that would mean an average voltage of 2.94 volts per cell. In the event that the current went to zero, then the - you'd have 29.2 which is still higher than that 26.5 which means eventually you're going to be reversing some cells. In the upper sketch there is the voltage times and the solid line shows the normal discharge. Now if one cell failed early - which is always the case - in parallel operation the other batteries could pick up the battery voltage in that particular stack would rise as the current went down. That shows the upper dotted line. The voltage on the other stacks or other batteries would go down because they are picking up more current. Eventually the voltage levels out and you have essentially one dead cell in each battery. That actually happened in our discharge test and there are at least two out of the four batteries that had cells that were driven so far in reverse that they would not recover the OCU. So that was our experience with batteries in parallel. It might be of interest to some of your applications. You will have a change in voltage as one cell goes dead and the other batteries will pick - up the load until you have essentially one dead cell in each battery.

Q. Halpert, JPL: Al were those thionylchloride cells?

A. Willis, Boeing: Yes.

Q. Halpert, JPL: And did you say what size they were incidently?

A. Willis, Boeing: 10,000 amphere hours - small ones.

Q. Halpert, JPL: Okay, so number one your comment is in your particular application if you have a very strong structure and if you have batteries in parallel you're safe. That's your contention at this moment and we won't push you any more on that. And there were some other people who said they had a safe design. Dave, you had your hand up. Would you be willing to talk for a moment on the issue?

A. Yalom, AT&R, Inc.: Everybody must recognize that a given battery must be designed for a given application. And if batteries are abused or misused, you're going to run into trouble. But I say that a battery can be made safe if it's designed for its end-item applications. That's what it boils down to.

Q. Halpert, JPL: I've got a lot of hands here. Anybody disagree with that. Well, I mean we have different kinds of tests. The Navy does heat tape tests. Are those cells safe if you blow them up like that? Are you satisfied with a cell if you see it blow up on a screen? Would you buy one of those? Well, where does safety begin and where does safety end? We're still in this bind and I'm trying to maybe separate out what it is we absolutely have to do to call it safe and what it is we're doing because we think we may have to do that to call it safe. There are a lot of people who felt that we have safe cells but you all didn't raise your hand. Does anybody else feel as though we can make a safe cell out of those systems?

Q. Levy, Sandia National Lab: If you make a cell for a specific application and the cell sees the conditions that it's supposed to see, that's one thing. But suppose this safe application gets involved in a fire or something. That's a whole other ball game. And how do you define safe? For instance, a $LiSO_2$ cell is designed to vent. If, in a certain application, it vents as it's designed to do is it considered safe? Or, does it have to not vent in the way its designed you know or just stay together? How do you define safe?

A. Halpert, JPL: Anybody want to answer that? Well, I think the comment about the application is certainly reasonable. It's got to be safe in the application. But, on the other hand, you have the two problems - one being the basic chemistry. Is the basic chemistry safe? And is the user handling it safe? That's where we have our problem and obviously why we don't want to use it in the consumer business. Because we know what people will do in the consumer business. But here we have military applications, we have aerospace applications and we have Burt Otzinger who wants to say something.

A. Otzinger, Rockwell International: I think one of the key items here is whether it is going to be used in close proximity to people or personnel versus using it in an application where personnel are not going to be imminently close to it. Because I think that, insofar as the lithium systems, what sets them apart from most other kinds of batteries is that the gasses that can come off when something goes wrong can be persinous or can cause real problems. If it weren't for that fact, I don't think it would be quite as big a problem. You can come up with your absolutely fail-safe system and so on and yet if you have a fire, a configuation or something - if it were to happen, say, in a spacecraft where they had no way

A. Otzinger, Rockwell International (Con't): to get out or do anything - as soon as the gasses evolved you've got a problem. It's a safety problem. So, how safe could you ever be in a situation like that. I don't think you ever can be. I think you're stuck. In some kinds of situations, a submarine - I think there are situations where because of the poisonous gas situation if you had some way to deal with that, then maybe you could finally say "Yeah, maybe we can handle that situation. But I think there are unmannered space probes - these kind of things where, sure, it could be made perfectly safe. I don't know about perfectly, but certainly safe.

Q. Halpert, JPL: Anybody else want to add to that? Feel free.

A. Taylor, Duracell International: Just to play the devil's advocate, I could argue that lithium managanese dioxide cells, lithium carbon monofluoride cells, lithium thinochloride cells are all safe - consumer safe. And the proof of that is that they are already available, all of them, in the consumer market place. I admit I've taken a bit of poetic license with thionylochloride, but I think that everybody is aware that union carbide, who talked about it last year, made these available in greater quantities. So, to make the statement deliberality, all three of those systems are available commercially already. You'll find managanese in your camera's shutter activating device. Though it's not a real time consumer application, you'll find carbon monofluoride in the Kodak disk camera. And I'm not quite sure where you'll going to find the thionylchloride, but it's coming. What does that mean? I think it means that lithium systems are going to have a commercial future and maybe it would be to some degree under definitions such as particular applications. Maybe that won't even be so in the future. I would hazard a guess that one or other, or more likely a range of them, are going to find commercial acceptance, never mind military acceptance. Because they can't do things other batteries cannot.

COMMENT

Gross, Boeing: I would like to, just for perspective, point out that the common lead-acid battery results in an order of two or three dozen explosions every year in this country, many of which cause a lot of personal injury and other kinds of damage. So, here is a battery that everybody considers safe, but yet, when it's misused or not used properly, it too can give us explosinos and unsafe conditions.

Frank, JPL: One understands the chemistry; one understands the thermal aspects of the system, followed up by quality control and handling, I think one can specify it safe for given applications.

Q. Otzinger, Rockwell International: One other issue - disposal. I tend to agree with the gentleman in that, yes, lithium cells are going to become more plentiful. I'm wondering how long it's going to be before disposal becomes a very serious problem?

A. Reiss, U.S. Army ERADCOM: We're buying considerable quantities of lithium sulfur dioxide batteries right now for the Army and for some of the other services. We have addressed the problem of disposal in significant efforts over the last three years. We have come up with certain conclusions to permit us to field the batteries are treated as a hazardous material. They are collected and centrally disposed of in secure land fills or hazardous waste land fills. It requires particular permitting for transportation to these sites. Within the military, we are going to be doing this through, routine contracts at each installation through the property disposal system. Each installation has one of these officers or works through a nearby installation. These people will be issuing contracts on a routine basis for the collection, not only of lithium batteries but of other hazardous wastes that are generated at the various installations, such as photographic wastes. It is a problem. We have come across particular scenarios that we are handicapped from a military point of view. When we got outside of the continental United States where batteries are airlifted in, totally in accordance with Department of Transportation rules and international rules. And yet when they are used they become a different item as far as the rules go and we can't put them back on an airplane to bring them out. We are addressing this problem right now. We do have certain controls within our system that will permit us to go on and perform our mission, but we think right now we're at a point where we can at least utilize the technology, utilize the various lithium densities. But there still has to be several issues resolved.

Q. Halpert, JPL: Okay, I would have to infer one thing from what you said to go back to your very first statement that you're buying large quantities lithium sulfur dioxide cells that you consider them safe. Am I supposing something that isn't safe for the application? What does your definition say?

A. Reiss, U.S. Army ERADCOM: As I implied, the Army has procured hundreds of thousands of batteries within the last three years alone in the lithium sulfur dioxide technology. We have used these batteries safely. We have used them in a variety of equipments. We have also had several problems. The statistics would show that we've had very few problems and I don't want to go into the numbers. We consider a dozen incidents too many out of 3 years. We are looking at military applications of these batteries. There has been some recent message traffic reporting, some of these incidents that are very disturbing to our commandus.

A. Reiss, U.S. Army ERADCOM (Con't): Words that we put into these teletypes say something like "the battery sounded like an incoming round when it ruptured." This is intolerable to an soldier. They cannot have batteries on their back or in their foxholes that are blowing up, or rupturing or venting or going "bang". Their purpose is to fight a war. They're not there to have their own equipment turn on them. And to that extent we feel yes the batteries have been used safely, but the safety record has to be improved.

Q. Halpert, JPL: I appreciate your making those comments off the cuff. Do any other people feel as though they have used or have applications where they really consider their SO_2, thionylchloride or BCX system safe or can be used in a safe application. Does that mean that every lithium SO_2, thianochloride or BCX cell is hazardous? Would you not use it? I think I beat it to death, huh. Well, we're frustrated - I'm frustrated, I shouldn't say we're frustrated. Maybe other people are frustrated too but I'm frustrated. I see a possibility of a real advance in the technology. We're talking about high energy density; we're talking about applications that would not be useful. I'll talk about the NASA mission, if you will where a man has a BCX cell in his helmet. And the only way he can get some decent hours out in the bay - out in the shuttle bay wondering around - is to have with him a cell of some kind so he can get enough amphere hours capacity so that he can see what he's doing. Otherwise he'd have to - he'd only have half an hour at the most by the time he got out and got back in.