

TESTING OF CANDIDATE BATTERIES FOR
GLOBAL POSITIONING SYSTEM

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ABSTRACT

Three lithium batteries which have been proposed as candidates for use in the Global Positioning System have recently been studied by Code R33 of the Naval Surface Weapons Center (NSWC). The batteries were discharged at several rates and temperatures both before and after environmental testing. Batteries were heated inside a closed chamber until they vented. Samples of the vented gases were analyzed, especially for components which might be toxic. The test results reported in this paper raise concerns about each of the proposed batteries.

INTRODUCTION

We were tasked to review three lithium batteries which were proposed by prime contractors for use in the Global Positioning System. The batteries are to provide "back-up" power for computer memory circuits within the system. Our review included the discharge characteristics of the batteries under a variety of conditions including discharge after vibration at low and high temperatures. Because the batteries may be used in an environment closed to the atmosphere, we obtained analytical data on the gases which were released when the batteries were heated until they vented. This paper summarizes the results of our study; additional details of this program will be available elsewhere.¹

The design characteristics of the three lithium batteries are listed in Table 1.

We purchased test lots of 100 of each of the candidate batteries directly from their manufacturers. The batteries were built to specifications developed by the manufacturers in conjunction with the prime contractors designing the Global Positioning System. As is clear from Table 1, the designs of the different contractors required batteries with different electrical characteristics.

EXPERIMENTAL PROGRAM AND RESULTS

The experimental program used for this project was very similar to our standard program which has been described previously.² After an initial inspection, we measured the open circuit voltage (OCV) and AC resistance (ACR) at 1000 hertz of each battery. Then the voltage under sequential

loads of 1000, 100, and 10 ohms was measured. The ACR measurements were then repeated. The results of these non-destructive tests are summarized in Table 2.

DISCHARGE TESTS

Discharge tests were run on three to five batteries of each type at both the four month and 24 hour rates. Studies at the latter rates were conducted at several temperatures and before and after vibration testing.

Low Rate Discharge

Room temperature discharge at the four month rate produced predictable, acceptable behavior from all three battery types. Voltages during discharge were quite stable until end-of-life for the $\text{SO}_2\text{Cl}_2/\text{Cl}_2$ and SOCl_2 systems. The voltage of the $\text{SOCl}_2/\text{BrCl}$ batteries dropped slowly from 3.9 volts at the beginning of discharge to a plateau of about 3.6 volts after one month.

Higher Rate Discharge

Room temperature discharge at higher rates also gave acceptable results. The voltage of the $\text{SOCl}_2/\text{BrCl}$ batteries under a 50 ohm load dropped from an initial value of 3.7 volts to a plateau value of 3.5 volts after a few hours. About 28 hours into discharge, the battery voltages began to gradually drop; but they did not reach the tests' 2-volt cut-off until after more than 50 hours of discharge.

Under a similar 50 ohm load, the $\text{SO}_2\text{Cl}_2/\text{Cl}_2$ batteries delivered a steady 3.3 to 3.6 volts at room temperature until about 48 hours into the test. Then their loaded voltages rapidly dropped to below one volt within 1 to 3 hours.

At ambient temperature, the SOCl_2 batteries delivered a steady 6.9 volts under a 200 ohm load for 24 hours. Their voltages then began to drop until they reached the experiment's 3-volt limit at about 30 hours.

Discharge behavior at 71°C was very similar to that observed at room temperature. As might be expected, loaded voltages increased one or two tenths of a volt over room temperature. The decline of voltage at the end of discharge typically began 1 to 3 hours earlier than at ambient temperature.

A temperature of -50°C had a marked effect on the discharge behavior of the three batteries. Under a 50 ohm load, the voltage of the $\text{SOCl}_2/\text{BrCl}$ batteries dropped from about 3.4 volts at the beginning of discharge to a value of 2.8 volts after 3 hours. The voltage remained at this plateau until it dropped to the experiment's 2-volt cut-off at about 23 hours. Thus these batteries delivered only about 40% of the ampere hour capacity realized at room temperature. Under the same low temperature loads, the voltage of the $\text{SO}_2\text{Cl}_2/\text{Cl}_2$ batteries dropped to zero and did not

recover during the 24 hour test; thus no capacity was recovered from these batteries at -50°C . The voltage of the SOCl_2 batteries at this temperature under a 200 ohm load never exceeded 3 volts and dropped to 2 volts after 24 hours. Since the minimum acceptable discharge voltage for this battery is greater than 3 volts, no usable capacity was available at low temperature even though there was some current flow.

Discharge Capacities

Discharge capacities were measured under several different conditions. Four or five batteries of each type were discharged at room temperature under loads of 50 or 200 ohms as described earlier. These discharges were completed within a month or two after we received the batteries. Twenty-four fresh batteries of each type were vibrated according to MIL-STD-810C at 71°C . Separate lots of 24 batteries were vibrated in the same manner at -50°C . After vibration, all of these batteries were discharged at room temperature using the same loads as in the previous tests. Because several months elapsed between the original discharges and the post-vibration discharges, five unvibrated batteries of each type were discharged as controls for the experiment.

The five, fresh $\text{SOCl}_2/\text{BrCl}$ batteries delivered an average of 3.48 ampere hours to a 2-volt limit. The capacities obtained ranged from 3.0 to 3.9 ampere hours. The capacities obtained from the 24 cells vibrated at 71°C ranged from 1.8 to 3.5 ampere hours with an average of 2.57. The cells vibrated at -50°C later delivered 2.0 to 3.6 ampere hours at room temperature; their average capacity was 2.82 ampere hours. The capacities of the five control batteries ranged from 2.5 to 3.6 with an average of 3.23 ampere hours.

The $\text{SO}_2\text{Cl}_2/\text{Cl}_2$ batteries gave similar results when discharged at room temperature through a load of 50 ohms to a 2-volt limit. The fresh cells' capacities ranged from 3.0 to 3.4 with an average of 3.14 ampere hours. After hot vibration, the range was 2.8 to 3.1 with an average of 3.01 ampere hours. The samples vibrated at low temperature yielded 2.7 to 3.2 ampere hours with an average of 2.95. The control samples varied from 2.7 to 3.0 with an average of 2.91.

The bobbin construction of the SOCl_2 cells in combination with an unwelded case gave rise to serious problems during discharge after low temperature vibration. Four fresh batteries discharged through a 200 ohm load at room temperature delivered 0.91 ampere hours capacity to a 4-volt limit with no significant variations. The capacities of the four control batteries discharged several months later ranged from 0.87 to 0.96 ampere hours with an average of 0.95. Of 24 batteries vibrated at 71°C , two delivered capacities of only 0.40 ampere hours while the capacities of the other 22 units ranged from 0.84 to 1.0 ampere hours with an average of 0.91. After low temperature vibration, only 6 of 24 batteries could deliver more than 0.8 ampere hours at room temperature. Five batteries had no usable capacity while the remaining samples delivered 0.1 to 0.7 ampere

hours. Upon inspection, we found that the cells in many of these batteries had leaked and that corrosion of the cell cases and connectors had occurred.

The discharge capacities are summarized in Table 3. The $\text{SO}_2\text{Cl}_2/\text{Cl}_2$ batteries exhibited a rather wide range of capacities, but capacity was not affected by vibration at either of the temperature extremes. The fresh $\text{SOCl}_2/\text{BrCl}$ samples had the same wide range of capacities, and these capacities were adversely affected by vibration. The unvibrated SOCl_2 batteries showed little variation in capacities; unfortunately, some of these batteries failed under high temperature vibration and 75% of the sample failed after vibration at low temperature.

HEATING TESTS

Fresh samples of each of the batteries were heated inside a 2.8 liter pressure vessel until the cells vented. Heating at about 20°C per minute was accomplished by wrapping each battery with electrical heating tape. During each test the temperature of the outside of the battery, the ambient temperature inside the pressure vessel, the battery's open circuit voltage, and the pressure in the vessel were monitored. For most experiments, the chamber contained air; but in some experiments, the air was removed with a vacuum pump, and the chamber was refilled with either helium or oxygen.

Each of the $\text{SOCl}_2/\text{BrCl}$ batteries failed with a loud "BANG" when the temperature of the battery's wall was between 200 and 300 degrees Celsius. The force of the battery failure was often great enough to rock the stainless steel chamber on its supports. When the batteries failed, the pressure in the chamber spiked to over 100 pounds per square inch gage (psig) except in the experiment in which the chamber contained helium. In this latter case, the maximum pressure recorded was less than 50 psig. When we opened the chamber after each experiment, we found that the cell cases had been ruptured and that their contents were scattered about the chamber.

Fresh $\text{SO}_2\text{Cl}_2/\text{Cl}_2$ batteries behaved in a manner generally very similar to that described for the $\text{SOCl}_2/\text{BrCl}$ samples, except that the events associated with battery failure were less violent. It is difficult to quantify the loudness of a report or the degree of case rupture, but the pressure spikes associated with the venting of these batteries were only half that observed for the first system.

The SOCl_2 batteries failed in a much more benign manner. As the temperature increased from 200° to 300°C , the two cells would vent quietly. Often the moment of cell failure could be identified only from slight increases in chamber pressure. The existence of two distinct pressure increases leads us to surmise that the two cells in these batteries often vented independently. The maximum pressure observed rarely reached 20 psig. Upon examination at the end of each experiment, we normally found the cells still intact in their battery case; the cells had vented through the end closed with the crimp seal, but the ventings were mild enough so that most of the cells' contents remained inside the case.

GAS ANALYSIS

Gas samples were removed from the pressure chamber after each battery had vented during the heating tests just described. These samples were taken in stainless steel pressure bottles to another laboratory for qualitative and quantitative analysis using gas chromatography and mass spectrometry.³ Several weeks often elapsed between battery venting and gas analysis, so the analysis would not be expected to identify any transient species.

The total amount of gas in the pressure vessel after a venting was calculated from the temperature and pressure data recorded during and after the event. We calculated the total quantity of toxic gases released by a battery venting by subtracting background gases (such as helium or nitrogen) and non-toxic products (such as carbon dioxide) from the total. We then assumed that these toxic gases would be evenly disbursed throughout a closed volume of 85 m³ (3000 ft³). We then calculated the concentration of these toxic gases in parts per million by volume. The results of these calculations for each battery tested are summarized in Table 4.

CONCLUSIONS

During this evaluation program, we identified several issues and concerns. We are very concerned about the safety of the SOCl₂/BrCl and SO₂Cl₂/Cl₂ batteries because their cell cases repeatedly fragmented during heating tests. The quantities of toxic gases released by some samples of the SOCl₂/BrCl battery under test conditions were also quite high relative to the other batteries. Concerns about capacity variability and performance at low temperatures of these two batteries have also been mentioned. The behavior of the SOCl₂ batteries is such that we are not overly concerned about their safe use in the Global Positioning System, but their performance after vibration and at low temperature causes serious concerns as to whether or not these batteries could meet all the requirements of the system.

REFERENCES

1. F. C. DeBold, James A. Barnes, R. Frank Bis, Susan Buchholz, Patrick Davis, and L. A. Kowalchik, Technical Report, Naval Surface Weapons Center, to be published (1984).
2. J. A. Barnes, R. F. Bis, F. C. DeBold, G. F. Hoff, J. D. Jensen, L. A. Kowalchik, and D. L. Warburton, 1983 Spring Meeting of the Electrochemical Society, San Francisco, Paper 2, (May 1983).
3. William Dorko, personal communication.

TABLE 1
BATTERY DESIGN CHARACTERISTICS

CELL CHEMISTRY*	CONSTRUCTION	CELL SIZE	CELLS IN BATTERY	VOLTAGE	CAPACITY
SOCl ₂ /BrCl	Spiral	AA	2 in Parallel	3.9 V	4 Ahr
SO ₂ Cl ₂ /Cl ₂	Spiral	AA	2 in Parallel	3.9 V	4 Ahr
SOCl ₂	Bobbin Crimp seal	2/3 AA	2 in Series	7.4 V	1 Ahr

*All cells contained lithium anode and carbon current collectors.

TABLE 2
NON-DESTRUCTIVE TEST RESULTS

CELL TYPE	OCV (Volts)	ACR (Ω)	LOADED VOLTAGE (Volts)			ACR AFTER LOADS
			1000Ω	100Ω	10Ω	
SOCl ₂ /BrCl	3.93	3.3	3.9	3.8	3.6	.55
SO ₂ Cl ₂ /Cl ₂	3.94	3.7	3.8	3.6	3.3	1.0
SOCl ₂	7.35	63.	7.0	6.5	5.3	2.4

Results represent the average value for measurements on 100 batteries of each type.

TABLE 3
AVERAGE CAPACITIES (AMPERE HOURS)

CELL TYPE	FRESH	AFTER VIBRATION		CONTROL
		HOT	COLD	
SOCl ₂ /BrCl	3.48	2.57	2.82	3.23
SO ₂ Cl ₂ /Cl ₂	3.14	3.01	2.95	2.91
SOCl ₂	.91	.91	*	.95

*Average not meaningful, see text.

TABLE 4
TOXIC GAS CONCENTRATIONS (PPM) CALCULATED
FOR A VOLUME OF 85 m³

BATTERY CONDITION	CHAMBER GAS	H ₂ S	HC1	SO ₂	CS ₂
PART A: SOCl ₂ /BrCl BATTERIES					
Fresh	Air	79	145	-	16
Fresh	Air	33	77	-	8
Fresh	Air	26	48	-	5
Fresh	Air	12	34	-	2
Fresh	Helium	7	15	.06	2
Fresh	Helium	7	25	.07	2
Fresh	Oxygen	8	24	.3	.4
Fresh	Oxygen	9	28	.3	.5
Discharged	Air	-	-	4	.2
Discharged	Air	-	-	6	.3
PART B: SO ₂ Cl ₂ /Cl ₂ BATTERIES					
Fresh	Air	1.0	7	.6	.8
Fresh	Air	.9	1	-	.2
Fresh	Helium	11	27	-	2.
Fresh	Helium	-	12	13	1.
Fresh	Oxygen	1.4	5	1	.6
Fresh	Oxygen	6.4	19	-	.4
Discharged	Air	-	.8	5	-
Discharged	Air	-	1	9	-
PART C: SOCl ₂ BATTERIES					
Fresh	Air	-	11	10	-
Fresh	Air	-	36	35	3
Fresh	Air	-	8	7	-
Fresh	Air	4	20	3	3
Fresh	Air	-	6	5	-
Fresh	Helium	-	8	6	-
Fresh	Helium	-	8	4	-
Fresh	Oxygen	-	2	3	-
Fresh	Oxygen	-	4	3	-
Discharged	Air	-	-	6	.1
Discharged	Air	.03	-	5	.05

- Q. Felder, General Electric: Why was there a - 54 degree requirement? For a communications system in a submarine that seems kind of low.
- A. Barnes, NSWC: The submarine people asked the same thing. In fact, the bigger and broader question is why do we need a backup with six month capability when, as we in the Navy recognize, a submarine loses power for six months, the memory is going to be a very small part of it. The current goal is to produce a common system for all services. And, therefore, there was a canvassing of all services to define the very worst possible use scenarios. And 54 degrees is a type of temperature that one might see in the Arctic. The high in temperature is a desert or sitting on a runaway in California type temperature. So the temperature extremes and the lifetime extremes were non-Navy driven. But then when they looked for the worst place to put this, they decided the submarine was perhaps the most restrictive environment which is why we ended up during the testing.
- A. Willis, Boeing: We have an application where we use a single AA BCX cell for memory retention. We have a six-month requirement and I notice your 24 hour rate. We use a 5,000 hour rate because that meets our application. In general we've had very good success with the test data on small sample lot and it looks like we're going ahead with that. It does not have the low temperature requirement. However, we have tested the PCX at intermittent periods of 93 degrees under that rate because of the desert application and found it still very satisfactory for that application.
- A. Barnes, NSWC: We have, in our test program, included 4 month discharge. But Jerry told me to limit this to 20 minutes, so I didn't bring all of the viewgraphs. I tried to pick representative ones.
- Q. Roth, NASA HQ: You used the term "remember these are only engineering items." Does that mean that these are better or worse than what you would get in production or what have you?
- A. Barnes, NSWC: I know that the folks from Electrochem Industries are standing here. I don't know about Union Carbide. I think you better ask them. What I did want to say was that I know from what I said this morning they are making changes - improvements - so I don't know what would happen if we got samples from them today. This is what happened to the small sample we got 15 months ago. Does someone EI want to make any other comment?
- Q. Cecil, Electrochemical Industries: The batteries that they used were production batteries. The assembly of the battery pack were engineering samples.

- A. Hodosh, Power Conversion: You made the statement that, after the work was done, you made a recommendation and it was sort of turned down because the user said they wouldn't use it under any circumstances. It's kind of like catch-22. I think I read you correctly and I imagine the reason for continuing and doing additional work is that you hope to convince the user, I guess eventually, that perhaps he should use it. I'd like to hear an end to that.
- A. Barnes, NSWC: As with all big systems - they're multiple level users. We are dealing with the electronics people who are developing the equipment. But they, in turn, must negotiate with the folks who are in charge of the various platforms. Because submarines are most restrictive, the people in charge of the submarine type desk were the people of most interest in these negotiations. At this point, the electronics people, that is, the people developing the GPS, are back talking, at the policy level, with the submarine people, weighing the relative merits of having anything that might release any toxic substance on the submarine as contrasted with the desire to produce a piece of equipment that will be common to all three services. And that's a policy-level issue. The submarine people's objection was categorical. They did not dispute our numbers. They did not question whether or not someone could survive if one of these batteries were to vent. They simply said, "you are talking about toxic materials. We don't think the need is great enough. Thank you very much." And or now it's a policy decision separate from our technical discussion.
- Q. Osterhoudt, Eastman Kodak: You said they rejected lithium batteries. Is lithium the villain or is it the cathodes?
- A. Barnes, NSWC: It was the toxic material.
- A. Osterhoudt, Eastman Kodak: You mean the cathode.
- A. Barnes, NSWC: The gases which were released when the battery vented, yes. I don't know how they would react if someone happened to propose a lithium battery that did not vent toxic materials.
- Q. Halpert, JPL: Jim, do I understand from your discussion that the heat tape test is a standard test for lithium cells for all applications or only for certain applications?
- A. Barnes, NSWC: The heat tape test is one of three tests called for in NAVSEA instruction 9310-1-A to be run on any lithium battery proposed, inside a piece of equipment, for a NAVY system. So, yes, the heat tape is a standard test. The other two standard tests are short-circuit and discharge in the voltage reversal and coming in the next revision of the instruction of the instruction will be a charging test as appropriate.