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High energy battery safety: anecdotes, issues and approaches

Julie A. Banner *, Clinton S. Winchester

Naval Surface Warfare Center, Carderock Division, White Oak Site, 10901 New Hampshire Avenue, Silver Spring, MD 20903, USA

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Abstract

The safety aspects of a battery's electrochemistry, design and manufacture can determine how, where or even if that battery may be used. Batteries that contain lithium require special consideration; the properties that make lithium useful for energy storage also increase the risks associated with its use. In this paper, safety issues for lithium and non-lithium primary and rechargeable battery systems are described. Historical anecdotes of battery safety incidents, both military and non-military, are presented. The US Navy's approach to lithium battery safety testing is also described.

Keywords: Safety reviews

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1. Introduction

Lithium batteries, both primary and secondary versions, are currently available for use in consumer electronic equipment. These batteries can be purchased off the shelf at many local electronics stores; they are usually found right next to traditional alkaline and nickel/cadmium products. Advertisers claim that your flashlight will burn brighter for a longer time, or your laptop will make it from coast to coast on one charge, when you use their product. However, recent news reports suggest that the product safety, particularly of rechargeable lithium-ion batteries, may benefit from further exploration. For example, a computer manufacturer was forced to recall their newest lithium-ion powered laptop due to internal fires caused by the batteries. Less than one month later, a major lithium-ion battery manufacturing facility in Japan was damaged by a fire that reportedly started in a battery storage room.

It should be noted that the cells involved in these incidents are consumer-oriented products engineered for safety, cost and performance. Accordingly, their energy density and power capability have been limited to maximize their safety characteristics. Military applications of lithium batteries usually require significantly higher energy and power densities than those achieved in devices designed for the consumer market. Scale-up of the lithium-ion technology to cell sizes and configurations which are suitable for military and electric vehicle applications is expected to intensify the safety risks associated with their use. Papers on investigations and experiments involving advanced intercalation materials and electrolytes document concerns for improving, or even maintaining safety while enhancing performance characteristics [1,2].

2. US Navy's Lithium Battery Safety Program

In order to mitigate the risks associated with fielding high energy power sources in the fleet, the US Navy developed a Lithium Battery Safety Program. In the late 1970s, the principal electrochemical systems under investigation for fleet use were primary (non-rechargeable) batteries with lithium foil anodes and sulfur dioxide or thionyl chloride catholytes. The Lithium Battery Safety Program was initiated in response to the significant number of safety related incidents with these early lithium-based primary cells involving ventings, fires and explosions, as tabulated by Bis et al. [3]. The first governing document for the Navy Lithium Battery Safety Program was NAVSEAINST 9310.1, dated 30 Mar. 1979.

As the quantity and variety of lithium batteries available for field use grew, the Lithium Battery Safety Program and its corresponding documentation expanded. The current version of the programme is contained in S9310-AQ-SAF-010, Technical Manual for Batteries, Navy Lithium Safety Program Responsibilities and Procedures, dated 20 July 1988. An updated version of this technical manual that specifically addresses the issue of safety testing of lithium rechargeable batteries is currently in the process of being published.

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* Corresponding author.

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3. Testing protocols and methodologies

A significant number of testing protocols for batteries exist. Some are directed at the consumer market, such as those developed by the Underwriters Laboratories Inc. (UL), the Japan Camera Battery group, and the International Electrotechnical Commission (IEC). As military requirements tend to be more stringent than consumer requirements, most branches of the military use their own battery testing protocols. The technical manual mentioned previously, known as '9310' for short, includes the US Navy's testing protocol for lithium batteries. The instructions and technical directives included in 9310 allow for the cautious and limited use of lithium batteries in Navy applications when and where they are appropriate. The restrictions found in the documentation are based on the assumption that a lithium battery represents a known potential hazard during its entire logistical mission-life, from the manufacturer's shop-floor, through mission use, to disposal. These restrictions direct the acquisition, use and deployment of lithium batteries as a function of chemistry, battery design, mission need and mission use-scenario. The critical requirement that must first be demonstrated is the absolute need for a lithium-based battery within the constraints of the mission design. Once it has been established that only a lithium-based battery chemistry can perform the mission, it is required that the proposed battery design contain the minimum amount of energy or power needed to meet mission requirements. Also, the particular lithium chemistry should be as benign as possible, while still capable of performing mission specifications. These constraints are of particular importance when battery packages are large (for either power or energy capabilities), or when the batteries are co-located with personnel and assets in such a manner that even minor accidents with the battery or equipment jeopardize the safety and health of personnel and survivability of assets.

The choice of a solid cathode chemistry (such as lithium/manganese dioxide or lithium/carbon monofluoride) over a liquid or liquefied gas cathode system (such as lithium/thionyl chloride or lithium/sulfur dioxide) is preferred, when mission performance is not critically impacted. In all of these chemistries, a series of abuses might cause a cell or battery to vent violently; however, a solid cathode cell will generally not have as immediate or as serious consequences as the other systems in the event of a minor leak or venting.

3.1. *Minimum test and performance requirements of 9310*

Technical manual S9310-AQ-SAF-010 lists the minimum number of specific tests that are required to be performed on a battery (or on a battery installed in a system) based on the nature of the battery and the system into which it is being installed. Battery types are organized into the following categories: active primary batteries, thermal batteries, reserve batteries, and secondary (rechargeable) batteries.

The five types of tests specified for active primary batteries are:

1. constant current discharge and reversal test
2. electrical safety device test
3. short-circuit test
4. charging test
5. high temperature test

The minimum tests prescribed for thermal batteries include:

1. unactivated environmental tests
2. high-rate discharge test
3. thermal abuse test
4. short-circuit test
5. charging test

Reserve batteries are required to be tested in the following scenarios:

1. unactivated environmental tests
2. unactivated high temperature test
3. activated constant current discharge and reversal test
4. activated short-circuit test
5. activated open-circuit test
6. activated charging test
7. high temperature activation test

Finally, secondary batteries require that a test plan which is specific to both battery and system design be submitted for approval prior to performing the testing. The test categories that should be included in any rechargeable battery test plan are:

1. short-circuit
2. high-rate charging and overcharge
3. high-rate discharge and reversal
4. thermal abuse

All of these tests must be conducted in triplicate.

The applicability of 9310 tests is dependent on the actual battery design. For example, if a battery consists of a single cell that is not connected to an external power source, there is no practical mechanism that would allow the system to charge the cell. Therefore, the charging tests would not be required, and could be waived in favor of conducting more meaningful tests to evaluate cell behavior within the system.

Also, modifications of these basic tests may be necessary to understand the behavior of the battery as installed in the system. For example, the tests described in the 9310 test procedures for active primary batteries are steady-state current tests; if a test article is actually used in a pulsed current application, the current profile in the test should be changed to reflect the behavior of the battery in the system.

At least some, if not all, of the above listed tests are required to be conducted in an enclosure that is representative of the final system enclosure. This is particularly pertinent if the system is designed to contain any or all of the gases and other products that might be released by a cell or battery during operational use, or in the instance of a cell venting. When it is appropriate and cost effective, the above tests may be conducted on exposed battery packages, with a final set of tests being performed on several batteries installed in a system, or a housing representative of the eventual end-item system.

Generically, 9310 stipulates the following constraints for a system to pass a containment requirement based on the use, carriage or deployment platform. By platform and location these criteria are as follows.

(i) *Land.* Fail-safe vent mechanism will operate to keep pressure below 50% of the yield point for the unit.

(ii) *Surface ship.* Same as (i), except there shall be no external flame or fire released when the vent mechanism operates.

(iii) *Aircraft.* Same as (ii).

(iv) *Submarine.* Total containment required. Generated internal pressures must remain below 50% of the yield point of the unit.

These criteria assume that lithium battery and lithium battery-powered equipment locations are in proximity to personnel or personnel air-space.

3.2. Additional test and performance requirements of 9310

The tests described above reflect the minimum number of explicitly described tests required for a lithium battery. These tests are typical of common situations that might arise during the use of a battery, regardless of battery design, manufacturer, system design or operation. These tests provide a foundation of sufficient information that is used to judge the safety risk of the battery in its given system. The results from these tests may also be used to recommend design changes or restrictions for limited battery use.

Additional or alternative tests may be desirable to evaluate system responses during various phases of the logistical life-cycle. These tests should be based on a detailed knowledge of the battery design, use environment, and possible accidents which might occur under plausible situations. One such example would be the effects of fork-lift tines penetrating a battery housing and piercing a cell or cells. Another example would be conducting an intermittent short-circuit ('soft' short-circuit), which can produce different behavior from the battery and battery safety devices than a 'hard' short-circuit. These additional tests, if they are required or requested, are usually identified with specific elements of a battery design, system operation, or logistical life-cycle. The test descriptions and guidelines included in 9310 were developed and written based on typical battery sizes of that time period. The largest of these batteries generally included no more than sixty R20/D-size cells in series or in series/parallel electrical configurations. Most of the early testing was conducted on batteries that were considerably smaller, consisting of two to five R14/C-size or smaller cells. Battery packages which are exceptionally large in cell size, series and parallel complexity, or overall energy storage require closer examination and modifications to the test program outlined above.

In some cases, particularly with large battery designs, characterization of the electrical performance and safety behavior of a smaller, isolated portion of the battery may be performed prior to conducting a definitive series of tests on the total battery assembly. This building block approach to testing permits the final battery-level and system-level tests to be optimized to understand battery behavior under abuse conditions in the system. The definition of a large battery may be based on either the number of cells in the battery, the complexity of the series/parallel connections, the size of the cells in the battery, or all of the above. The performance and safety characterization of cells or sub-module battery strings is conducted so as to reduce the test risk (and costs) at the battery-level, while reflecting the test conditions of the larger battery in a more controlled and observable arena.

4. Some examples of safety issues for various batteries

As noted in the testing protocol discussion above, a battery's safety characteristics depend strongly on many variables; these variables include (but are not limited to): cell chemistry, cell construction, and battery construction (including both mechanical and electrical design factors). In this section, we will attempt to outline some general trends regarding battery safety. We will use specific examples of actual battery events to illustrate these trends.

Abusing a lithium/sulfur dioxide battery by charging it can cause extremely violent reactions, including venting of the battery accompanied by flame. It is not unusual under these circumstances for cell and battery housings to be torn apart, resulting in shrapnel. Recently, a US Army sergeant was injured in an accident involving a lithium/sulfur dioxide battery known as the BA-5590. The battery was installed in his portable global positioning unit, which was connected to vehicle power in his HMVEE. The preliminary explanation for this violent venting was that the battery was inadvertently charged by the vehicle's starting-lighting-ignition (SLI) battery.

Discharging a lithium/thionyl chloride cell or battery into voltage reversal at a low temperature, such as 0°C, can result in inefficient use of the lithium during the discharge, and the formation of lithium dendrites and metastable species during the voltage reversal. Allowing a cell or battery that has undergone this type of abuse to slowly warm to room temperature can result in violent venting, as the active materials left in the cell begin to react as the temperature increases. Testing of large (> 2000 Ah) lithium/thionyl chloride cells in this manner has resulted in the complete demolition of the commercially manufactured chest freezers that were used as temperature chambers for the experiments.

The reactions of thermal batteries to abuse scenarios tend to be design and size dependent. Activating a thermal battery into a no-load situation, known as the open-circuit test, often results in internal short-circuits of high-rate or long-life battery designs. Once an internal short-circuit between the anode and cathode occurs, thermal runaway usually results. Because these batteries function at very high temperatures, the outcome of thermal runaway may involve molten stainless steel as the battery case is melted from the inside out. During open-circuit and short-circuit tests of a standard thermal battery used in a missile application, the reactions of the batteries were sufficient to melt through the external housing of the missile on multiple occasions.

The riskiest time in the life-cycle of a reserve-activated battery is usually at the moment that the electrolyte is first introduced into the battery. Because this type of battery is usually designed to undergo electrolyte fill after it has been installed in a system or weapon, this act of filling becomes a major concern for the user community. If any design flaws exist, or misassemblies have been made, they can show up quite violently at this critical time. A large, reserve-activated, lithium/thionyl chloride battery that was built with deliberate short-circuits across some of its cells exploded upon activation with enough force to lift a 13 tonne test chamber more than 2 m off the ground.

Rechargeable batteries have a challenging life-cycle with respect to safety, due to the need to control properly such variables as recharge voltage, charging current and duration, discharge cut-off voltage, and accumulated cycles. As mentioned in Section 1, consumer lithium-ion batteries have been involved in publicly reported safety events involving overheating and igniting. Even non-lithium rechargeable batteries can react violently given the right (or wrong) circumstances. A large silver oxide/zinc battery that had been designed for use in a mine application overheated, caught fire, and burned out of control for more than one hour after being activated with an excessively reactive electrolyte.

The primary hazards from some non-lithium batteries derive more so from the active materials used in them, than from the violence of their venting behavior. Batteries comprised of mercuric oxide/zinc button cells can overheat and vent in response to an external short-circuit. Although the cells are small, and unlikely to cause significant damage from shrapnel, one such event involving a few vented batteries resulted in the evacuation of a building and a $0.5 million clean-up programme to remove the mercury contamination from the area.

5. Conclusions

Batteries provide necessary energy storage capability for myriad applications. However, when that energy is released in an uncontrolled manner, they can be extremely dangerous. The US Navy has enjoyed an excellent safety record since the implementation of the Lithium Battery Safety Program documented in NAVSEAINST 9310.1B and the technical manual S9310-AQ-SAF-010. The challenge for the future is to maintain this safety record while advancing technical capabilities through the use of new and improved battery designs.

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