Battery Safety Qualifications for Human Ratings

by Judith A. Jeevarajan and Clinton S. Winchester

The battery qualification process for the use of batteries for human-rated space and Navy missions follows a very stringent protocol. Certification involves extensive cell-level as well as battery-level testing in the relevant environment. Unique requirements such as vacuum and extreme thermal environments, beyond a traditional manufacturer's specification for the cell, lend to additional testing at the cell and battery levels to confirm safety.

Electrochemical energy storage (batteries) and conversion systems (fuel cells) have been used as main power sources for space vehicles and satellites for a long time. Rechargeable batteries have predominately been based on lower energy density, aqueous electrolytes. However, with the advent of the use of lithium-ion batteries for powering space vehicles and satellites. the need to understand their hazards in battery configurations much larger than portable electronic equipment applications, has become mandatory. At NASA-JSC, a process to certify these batteries is used that takes into consideration the application. environment, battery voltage and capacity, and period of usage including the storage periods. All batteries that react to an offnominal condition in a catastrophic hazard nature in a crewed environment require twofault tolerance. This is the top-level NASA safety requirement for the International Space Station (ISS)¹ and other humanrated space applications. The crewed environments include those that are attached to habitable volumes as well as those used in launch vehicles of human-rated spacecraft. The U.S. Navy employs a similar but different set of standards and criteria for examining and characterizing hazards of lithium-based batteries and high-energy chemical power systems. This paper is written with a special focus on the lithiumion battery chemistry and associated hazards with its use in manned environments and unmanned systems interfacing with manned platforms.

Certification Process

Battery Safety and Hazard Categorization.—Battery Safety is based on the reaction of a particular battery to an abusive situation. The abusive situation predominantly arises in an inadvertent manner. To account for the safety of the battery under different abusive conditions, test data are required. Because these data are typically not readily provided by the cell or battery manufacturers, testing the cells and batteries is required.

Certain chemistries of batteries have very high energy content and need to be handled with the required precautions. For example, the stoichiometric energy of lithium-thionyl chloride cells, (expressed as watt-hours/kg) or other Li/oxyhalide systems, exceeds the equivalent mass of TNT. Figure 1 shows the underwater displacement bubble from a single D-size lithium-thionyl chloride cell that was subjected to a 3% capacity overcharge abuse. The diameter of the bubble characteristics allows determination of the instantaneous energy released.

These chemistries can yield close to 50% of theoretical electrical energy release in a single 20 to 50 millisecond event. Cells and batteries with aqueous electrolytes, like potassium hydroxide, can produce hydrogen and oxygen gas under overcharge and overdischarge conditions. These gases can explosively combine to produce water. Other battery electrolytes such as organic solvents are flammable and can ignite in the presence of oxygen which can, in many cases, be formed in the cell due to decomposition or release of oxygen by the cell components. Exemplar chemistries include lithium-ion cells using metal oxide cathodes and lithium primary cells with manganese dioxide with or without perchlorate salts.

Hazard categorization at NASA is primarily based on the toxicity level of the electrolyte that leaks in the event of a battery failure. Inadvertent abuse of the cells or batteries can also result in the cell or battery venting and electrolyte leakage. Details of toxicity categorization at NASA-JSC can be found in JSC 26895² and that for batteries can be found in JSC 25159.³ Although the latter document was written for Space Shuttle mission environments, the concept has been extended for other human-rated space environments including the ISS.

Toxicity categorization is based on the toxicity of the electrolyte and the clean up capability for a specified habitable volume.

For batteries this categorization can range from a 4 to 0, with the exception of 3, which is for chronic health hazards due to damage of internal organs. Aqueous electrolytes in most battery chemistries that utilize them are made up of concentrated potassium hydroxide which is typically at Tox-2 category. Due to their poor ionic conductivity, organic solvents typically have dissolved inorganic salts to increase that conductivity. The salts used in the organic solvents are typically of Tox-2 category. Some aqueous electrolyte systems, as in lead acid batteries, use a concentrated sulfuric acid electrolyte and are also of the Tox-2 category. A failure that causes leakage of a Tox-2 or higher category electrolyte or vapors, and/or causes fire, explosion, or thermal runaway is categorized as catastrophic and requires twofailure tolerance (see below, "Documents for Battery Requirements").

A failure modes and effects analysis (FMEA) is first formulated for any battery design and the hazards assessed using this process. Controls are designed with the two-failure tolerance to catastrophic hazards approach. For those failures where external controls cannot be provided (*e.g.*, internal shorts) a design for minimum risk approach is used, which includes combinations of screening techniques to minimize the hazard.

The U.S. Navy presently uses a combination of hazards characterizations based on the design of the system, battery, battery chemistry, and potentially imposed environments over the life of a battery in a system application.

The Navy also distinguishes hazard characterizations based on location for manned systems and operation, size of the energy storage system, known failure histories and other factors such as co-located

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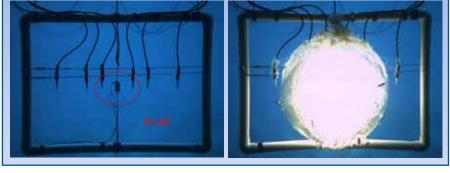


FIG. 1. Underwater test of a Li/SOCl₂ cell to characterize work conducted by failure. The image on the left shows a lithium thionyl chloride "D" cell suspended underwater. The image on the right is taken 20 milliseconds after a triggered casualty. The "bubble" is approximately 30" at maximum extent. Cell yielded over 30% of the practical cell electrical energy as an abrupt thermal and pressure event. Pressure shock sensors are located near the cell.

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energy systems and potential environments, as well as potential toxicity and secondary fire initiations in the event of a battery failure.

Hazard characterizations associated with a large battery (greater than 1 kWh electrical), intrinsically toxic chemistries (SOCl₂), or extreme flammability of electrolytes, require special review and considerations if carried internal to a ship, submarine, or aircraft. Particular attention is paid to exceeding IDLH (immediately dangerous to life and health) characteristics of electrolytes and decomposition products as well as potentials for overwhelming fire-events from flammable electrolytes or fuel-air ignitions that may exceed local pressure ratings. The impact of external shock and pressure are also of concern in characterization of hazards.

Documents for Battery Requirements.— At NASA-JSC, the battery requirements document, JSC 20793, titled "Crewed Space Vehicle Battery Safety Requirements³⁴ is used to assess safety of the batteries designed for various applications including space vehicle batteries. The "Battery Processing" document, JWI 8705.3,5 goes hand-inhand with the JSC 20793 as it provides the hardware owner the information on processing batteries from start to finish. The document clearly states the roles and responsibilities of all the members of the team including those for the hardware owner, battery user, battery expert, other experts, and the safety and mission assurance support team. The document requires that hardware owners think about the choice of batteries, pre-flight processing, on-orbit processing, and post-flight processing of the batteries, wherever applicable.

The U.S. Navy currently uses two basic technical evaluation documents for lithium battery safety. These are NAVSEA Technical Manuals S9310-AQ-SAF-010 "Technical Manual for Batteries, Navy Lithium Safety Program and Procedures, Rev 2" and SG270-BV-SAF-010 "High Energy Storage Systems Safety Manual." These documents are limited to lithium and lithium battery systems and also invoke several cited additional documents as required for the characterization and evaluation. MIL-STD-882 (System Safety Program Plan), and Naval Ship Technical Manual (NSTM) 555 (Fire Protection) are examples of secondary guidance used in these evaluations.

These documents cover the entire range of battery and energy storage systems from coin cells, to man portable and ship recoverable equipments, to embedded ship battery systems that may be many thousands of liters in volume. Whereas NASA engineering philosophy is a system to be two-fault tolerant and safe, the Navy criteria is a single fault tolerance within the confines of a system, or sub-system. Life critical systems require additional levels of redundancy for safety that include fault

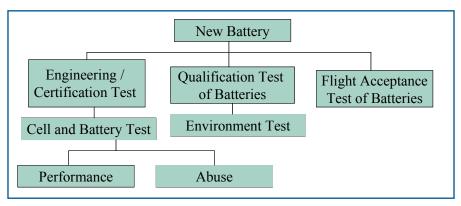


FIG. 2. Simple schematic of the battery certification process for space missions.

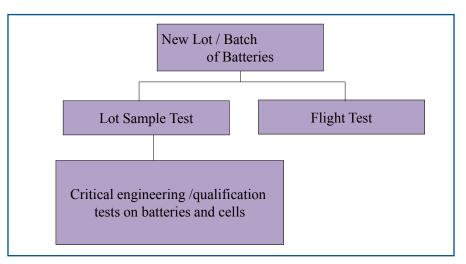


FIG. 3. Simple schematic of lot acceptance for every new lot of an existing certified battery.

indication and determination of maximum credible event, maximum credible platform casualty and worse-case event.

NASA Battery Certification

The battery certification process at NASA-JSC includes three main phases. They are the engineering, qualification, and flight acceptance phases and all three are very critical for the safety certification process. Lot sample testing is required for every new lot manufactured for a flight program to confirm that each new lot has the same performance and safety characteristics as was originally determined. Lot sample testing will not be required in cases where only one lot is being used for flight and all the testing has been carried out with adequate samples from the same single lot. Figures 2 and 3 provide simple schematics on the process used for the certification of batteries.

Engineering Design/Test Phase.—The first part is the engineering evaluation of the batteries which includes cell as well as battery level testing. These tests are carried out to determine the performance as well as safety characteristics of the cells as well as the battery configurations. Initially, cells from different manufacturers are purchased and tested to determine their performance and safety characteristics. Following this,

a suitable candidate cell is chosen and the process of battery design is initiated. In the engineering design and test phase, cell level tests, as a minimum, include rate capability, pulse capability, performance at different temperatures, determination of vent to burst ratio, as well as their safety tolerance under conditions of overcharge, overdischarge into reversal, external short, simulated internal short,⁶ and extreme temperatures.

The NASA-JSC approach regarding the tolerance of a cell design to an internal short hazard does not reject or disapprove any cells due to the resultant thermal runaway behavior. The results are used to determine the best method to mitigate or screen the cells from internal shorts. At NASA-JSC, the cell designs that undergo thermal runaway are categorized as "intolerant to internal shorts," whereas those that do not exhibit thermal runaway are "tolerant to internal shorts." A vibration screening process, along with a stringent flight battery acceptance test program, is carried out to screen cells and/ or batteries for internal short defects. This method has been used as an approach in designing the batteries for minimum risk since no external controls can be used to protect a battery or cell against an internal short

The battery level tests include testing under the relevant mission and launch performance loads as well as thermal and pressure environments. Thermal analysis is carried out to determine the thermal gradient within the battery and designs for the lowest acceptable thermal gradient within a battery module is chosen. Unique environments such as vibration during launch or on-orbit as well as impact loads during landing are also to be taken into consideration during the design phase, and the structure built to accommodate such unique requirements. Batteries may have restrictions on both mass and volume which need to be taken into consideration when the battery is designed.

Safety tests at the battery level, as a minimum, include overcharge, overdischarge, and external short tests. It has been well established through years of testing at NASA-JSC that cell-level controls do not translate into battery-level controls. Controls, especially those internal to the cells, have shown to not protect or themselves be the cause for hazardous events due to their limitations.7-10 Safety tests are also to be carried out in the relevant environment. NASA-JSC test programs have indicated that safety tests under ambient pressure conditions display results contrary to that in a vacuum environment.¹¹ A cell or battery's safety tolerance up to the settings of the safety controls are verified by safety tests.

Lots sample testing is carried out when subsequent/multiple lot are procured/ manufactured for any flight program. Random samples of 3 to 6 % of the lot are subjected to critical performance and safety tests. This is to confirm that the safety tolerance of the cells remains the same for the subsequent new lots of cells manufactured.

Qualification Phase.—The second phase of the certification process includes qualification testing. Qualification testing, as a minimum, includes testing a flight-like battery for performance to the required flight environments with a margin imposed.⁴ The flight-like battery is a high-fidelity prototype that is identical to the flight battery in design. This test is typically carried out on only one qualification battery unless the schedule requires multiple tests to be run in parallel due to time constraints. The environment and margin are determined by the project team and are provided in the project specification for the cell and battery. The performance tests include mission profile protocols under the relevant pressure (intra-vehicular is ambient pressure and extra-vehicular is a deep vacuum environment) and thermal conditions as well as vibration to the required spectrum for a specified duration, where both the spectrum and duration provide a margin over the flight environment. For those cell/battery chemistries or designs that are intolerant to an internal short (result in violent venting, fire, thermal runaway), the batteries are screened for internal shorts using a level of vibration that is higher than that required for workmanship screening. Hence, those batteries are tested to a spectrum that has

Flight Acceptance *Phase*.—Flight acceptance testing is carried out on 100% of flight batteries. The flight acceptance phase starts with cell screening where 100% of the cells undergo physical examination, dimension, and weight measurements, open circuit voltage, capacity and internal resistance, and/or ac impedance and self discharge tests. Cells are then matched based on voltage, capacity, and internal resistance, and built into modules. Where required, screening of cells may include high-resolution X-rays to confirm the absence of foreign or native contaminants, electrode alignment, weld integrity, etc. The flight batteries then undergo flight acceptance testing that includes, as a minimum, performance testing (charge and discharge cycles), followed by vibration, post-vibration performance comparisons, vacuum or thermal vacuum leak checks, followed by post-vacuum comparisons. For those cell/battery chemistries or designs that are intolerant to an internal short (result in violent venting, fire, thermal runaway), the batteries are screened for internal shorts using a level of vibration that is higher than that required for workmanship screening.4 As with qualification tests, the pass/fail criteria are stringently imposed to screen out any failures. The pass/fail criteria include comparison of open circuit voltage, capacity, mass and internal resistance, and/ or ac impedance.

The data collected from the three phases, along with any relevant analysis and other documentation, are submitted in the form of a safety data package to the relevant NASA safety panel to obtain final safety approval for flight.

U.S. Navy Battery Safety Assessments

The basic premise for the U.S. Navy's Lithium Battery Safety and High Energy Chemical Storage Safety programs is full containment of all possible reactions and resulting material releases and energy releases, or the complete assessment of hazards and determination of and mitigation of these risks. Failing these, a determination of acceptability of risk and likelihood based on mission needs must be made at the appropriate level for the platform and mission.

Like the NASA efforts, a fundamental performance verification and environmental survivability is needed before a lithium or lithium-ion battery system may be

considered to be fielded. This is conducted based on established environmental specifications developed by the program for the operation of the system using the battery. For shipboard systems, this would include vibration and handling while exposed to extremes of temperature. For aircraft systems, this includes flight worthiness demonstration tests including aircraft vibration, temperature, and effects of limited aircraft crash g-loads. For unmanned underwater systems (UUV), withstanding applied pressures is required. These tests are required before a system may be deployed in operation or demonstration tests, but may be conducted in parallel with Navy safety evaluations and risk of use assessments.

NAVSEA Technical Manual S9310-AQ-SAF-010 was established in the late 1970s to address lithium battery safety. The focus of this document includes all ground, air, surface, and sub-surface use and operation of lithium and lithium-ion batteries by Navy personnel and in Navy platforms or facilities. This document has been adapted for use of cells and battery systems from coin-cell to multi-hundred kilowatt-hour systems that range from portable man-wearable sensors to large unmanned autonomous underwater vehicle using both lithium-primary and Liion rechargeable chemistries.

Principal characterization of this document is the evaluation of electrical safety of the battery under a series of electrical abuses that pre-date many of the current UN/DOT. IEEE, IEC, SAE, UL, and ASTM standards. Battery responses, as battery alone and as part of a system assembly, to overcharge or excessive overvoltage, forced discharge or overdischarge, cyclic over-charge and over-discharge, and short-circuit, all applied with and without internal electrical safety devices are measured and determined. Additional failure modes associated with exposure to high temperature (targeted as 500°C) are characterized as well. Additional conditions applied include specific shipboard and aircraft shock conditions especially for battery systems that utilize a battery monitoring and management system to communicate to the host platform that are considered critical to function after the event as the shock may cause systemic damage across electrical and physical interfaces. Figure 4 illustrates a sequence of images from a S9310-AQ-SAF-010 induced failure and propagation of a lithium-ion commercially built battery pack subjected to limited triggering abuse on one section of the overall pack. The battery is comprised of 84 cylindrical li-ion cells in parallelseries connection. The reaction sequence eventually consumes the entire battery.

The second document, TM SG270-BV-SAF-010, was established after a severe battery fire damaged a platform in 2008. Although the battery and platform had undergone evaluation in accordance with NAVSEA TM S9310-AQ-SAF-010, the severity of the fire and damage initiated

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Navy-wide standdown in lithium battery assessments and approval for use until a more robust system was established. The SG270-BV-SAF-010 also evaluates failures of lithium batteries to known abuse conditions, but extends the assessment to determine system and platform reactions with some level of quantitative measurements, predictive hazard assessments, and test and evaluation of mitigative processes, systems, and controls. The measurements include rate of heat and pressure release, rate of gas release, primary battery and secondary battery induced heat release as thermal flux and total convective emission. Table I is a sample table taken from SG270-BV-SAF-010 and details both the type of evaluations conducted and the level these characterizations are applied along the continuum of cell, to cell-pack, to module, to full battery assembly.

Prescriptively, the tests are applied on the basis of a thoroughly detailed operational system and platform logistical scenario as documented within a preliminary hazard assessment that focuses on the primary hazards from the battery for the system. Battery and cell failure response characteristics are measured and assessed either through techniques applied as structured in the prior \$9310 document or by specific application of triggerable internal faults or limited triggered cells within a battery pack. Mitigation techniques, procedures and platform suites of systems, and command/control communication sensors are detailed and designed to manage a battery failure, and these are then tested. Only if a severe explosion or fire are still considered likely with a platform or programmatic impact of major or critical after all mitigations are applied does the system undergo a risk acceptance authority review to assess criticality of need. Systems that meet the former or latter tests are allowed into use.

Heat release is tested and characterized using various combustion calorimetric systems and standards such as ASTM-1354. Gas releases and toxicity are characterized using atmospheric contamination standards that can be traced to EPA standard tests. These are based either on real-time sampling and measurements or sample collection bottles. Fragment impacts and pressure pulses are characterized through appropriate means including witness plates and impact sensors. Platform mitigation responses and specialized design suite systems are implemented and tested to reduce effects of the unmitigated characterization on platforms. Figure 5 depicts a small-scale oxygen consumption calorimeter often referred to as a cone calorimeter with the primary functional elements and a test for combustion reactions of a laptop lithium-ion pouch cell reacting to stimulus. Data from the cone calorimeter allows sizing of fire protection equipment for shipboard systems.



FIG. 4. Failure sequence of a commercial Li-ion battery (clockwise from upper left).

Table I. Table from SG270 for characterization of battery casualties.					
Battery Casualty Hazard Characterization Test		Cell-Level BCCT	Intermediate Module-Level BCCT	Full-Scale Assembly-Level BCCT	Platform Hazard Characterization and Mitigation Verification
5.2.1.2	Quantitative Off-Gas Production Analysis.	x			
5.2.1.2.1	Real-time and Continuous Monitoring of Gases.	X			
5.2.1.2.2	Grab Samples for Toxic and Corrosive Gases.	X	X	X	X
5.2.1.3	Volatile Off-Gas Ignition.	X	X	x	X
5.2.1.2.4	Thermal, Volametric, and Pressure Impacts of Off-Gas Ignition.		X	X	X
5.2.1.2.5	Gas Velocity Measurements.		X	x	X
5.2.1.6	Heat Release Rate and Thermal Flux.	X	X	X	X
5.2.1.7	Pressure and Pressure Transients.	X	X	X	X
5.2.1.8	Incandescent Debris and Shrapnel.	X	X	x	X
5.2.1.9	Aerosol Analysis.	X			
5.2.1.10	Smoke Generation.		X	X	X
5.2.1.11	Metal and Material Exposure.	X	X		
5.2.1.12	Cell Failure Propagation Tests.		X	X	X
5.2.1.12	Mitigation Verification Tests.		X	X	X

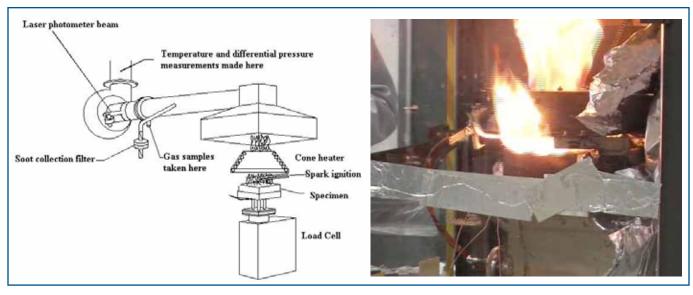


FIG. 5. Oxygen cone-calorimeter test of a Li-ion pouch cell to determine heat release rate and total energy.

These are done based on objective quality evidence that is quantitative. This is the most significant change from earlier S9310 characterizations that established the existence of a platform hazard qualitatively but might not have established sufficient quantitative data to allow a program or system designer to effect hazard reduction and mitigation with objective quality evidence of successful management.

Future Evolution and Developments

The SG270-BV-SAF-010 High Energy Chemical Storage Safety technical manual is currently written around lithium battery designs, including primary lithium chemistries, lithium-ion chemistries, and future lithiummetal rechargeable systems like lithiumsulfur. SG270 is also applicable to nonbattery supercapacitor, fuel cell, semi-cell, and sealed system chemical thermal energy conversion systems (*e.g.*, aluminum or lithium combustors) where extremely high energy densities are reached (400 to 1000 Wh/kg) with complications of significant balance of plant supports are necessary.

Summary

The process used to establish the safety of batteries required for NASA space vehicles and U.S. Navy requirements for systems that support human-rated systems or manned support platforms has been described in a simple manner in this paper. Due to the nature of the catastrophic hazards induced by bad cell and/or battery designs, it is imperative to design stringent controls to prevent such hazards from resulting in a loss of crew, platform or mission. Testing using the relevant design configuration and environment is crucial to obtaining a safe battery for use in a human-rated environment.

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References

- 1. SSP 50021, Section 3.3.6.1.1 Safety Requirements Document for ISS.
- JSC 26895, "Guidelines for Assessing the Toxic Hazard of Spacecraft Chemicals and Test Materials," October 1997.
- JSC 25159, "Toxicologic Hazard Assessment on Batteries Used in Space Shuttle Missions," August 1991.
- J. A. Jeevarajan and E.C. Darcy, JSC 20793 Revision B, NASA-JSC, 2006.
- 5. J. A. Jeevarajan, JWI 8705.3, 2011.
- J. Jeevarajan, T. Viviano, H. Jones, T. Chapin, and M. Tabbador, Proc. of the 2011 NASA Battery Workshop, November, 2011.
- J. Jeevarajan, E. Darcy, G. Varela, F. Davies, and P. Patel, *Proc. of the 43rd Power Sources Symposium*, July 2008.
- W. A. Tracinski and J. A. Jeevarajan, *The 2006 NASA Battery Workshop*, Huntsville, AL, 2006.
- 9. J. A. Jeevarajan and P. Patel, *Proc.* of the 2007 Space Power Workshop, Manhattan Beach, CA, 2007.
- J. Jeevarajan and W. Tracinski, *The* NASA Battery Workshop, November 2008.
- J. Jeevarajan, B. Strangways, and T. Nelson, Proc. of the 2011 NASA Battery Workshop, November, 2011.
- 12. J. Banner and C. Winchester, *J. Power Sources*, **65**, 271 (1997).
- C. Winchester, J Banner, D. Fuentevilla, J. Govar, and J. Barnes, 25th International Lithium Battery Seminar, March 2008. "Large Format Li-Ion Batteries: Use, Abuse, Testing and Safety Concerns: A U.S. Navy Perspective."