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Oak Ridge National Laboratory Lithium-Ion UPS Battery Research and Commentary

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ABSTRACT

Lithium-ion batteries are increasingly prevalent in a variety of devices both small and large. The high level of stored energy in UPS battery racks is closely scrutinized because sudden, uncontrolled release of chemical and electrical energy could be an ignition source. Because of this concern, lithium-ion battery safety is the subject of several testing standards, including UL 1642, UL 1973, and UL 9540A.

The motivation for this research and commentary is the potential installation of lithium-ion batteries in a Vertiv UPS assembly for one of the buildings on the ORNL campus. The battery modules Vertiv uses are compliant with abuse survival testing, demonstrating that cells and modules are rugged. The modules are further compliant with fire propagation requirements – in the event a failure does produce a fire, it does not spread. Beyond these, the rack level assemblies Vertiv sources comply with UL requirements to contain a fire within the rack.

This three-tiered approach to battery safety suggests Vertiv's lithium-ion UPS battery racks can reasonably be considered for use in a facility with appropriate fire protection provisions and an informed emergency response team.

1. SUMMARY OF HAZARDS PRESENTED BY LI BATTERIES

Lithium-ion batteries, as a general category, have been used in high density energy storage systems (ESS) since the early 1970s. While there have been any number of sensational reports of fires caused by these cells, particularly in consumer devices, many are the result of physical damage or abuse with a lesser number directly attributable to cell flaws.

1.1 FIRE

Lithium-ion battery fires are a concern for conventional reasons. The various electrolyte mixtures contain hydrocarbons that are themselves combustible, and that degrade to short-chain hydrocarbons which may be explosive. The plastics used in cell and module assemblies will burn. The electrolyte and plastic cell or module case may include compounds containing fluorine which produce hydrogen fluoride (HF) as a combustion product.

Lithium-ion batteries represent a unique fire hazard because the high level of available chemical energy can directly produce an uncontrolled exothermic reaction. Electrical current, normally the desired end-product of the battery, can flow internally and significantly accelerate an already out-of-control release of heat.

1.1.1 Explosive gases and liquids

Thermal destruction of lithium-ion batteries can produce and release several combustible, flammable, or explosive gases and liquids.

- Hydrogen
- Ethane, methane [1, 2].

Lithium battery cathodes produce oxygen, an accelerant.

1.1.2 Corrosive and toxic gases and liquids

Igniting lithium-ion batteries produces several corrosive and toxic products of combustion.

- Hydrogen fluoride arises from decomposition of electrolyte and the plastics used in enclosures.
- Alkyl carbonate (electrolyte solvent) is vaporized and released.
- The burning process directly yields carbon monoxide, carbon dioxide, POF_3, noxious soot and other combustion products of the plastic housings.

HF generation from combustion of lithium-ion cells is limited below 170°C. Additionally, because HF is highly water soluble, conventional deluge fire suppression limits personnel exposure to this toxic and corrosive gas [1].

Sturk, Hoffmann, and Tidblad have shown that for lithium-iron-phosphate (LFP) batteries, the electrolyte decomposing yielded HF and PF_5 accumulation in cells above those already ignited, resulting in these gases being vented prior to the cells or modules catching fire. By contrast, Sturk et al found burning lithium-nickel-manganese-cobalt oxide (NMC) cells produce less HF gas, over a shorter time, than LFP cells under similar conditions.

2. TYPES OF CHEMISTRIES

Lithium-ion battery anodes usually consist of graphite and a binder material.

Cathodes in modern lithium-ion batteries are typically a combination of small amounts of lithium metal mixed with various other metals and metal oxides. These combinations include lithium-cobalt oxide, lithium-iron-phosphate, lithium-manganese oxide (LMO), lithium-nickel-manganese-cobalt oxide (NMC), and lithium nickel cobalt aluminum oxide (NCA).

Electrolytes vary but are conventionally an organic (methyl- or ethyl-) carbonate [2] and lithium hexaflurophosphate ($LiPF_6$) [3].

2.1 LIKELIHOOD OF THERMAL RUNAWAY OF EACH CHEMISTRY AND CAUSES

The self-accelerating exothermic reaction called "thermal runaway" can occur at different temperatures, depending on the cell materials and construction. **Because a variety of conditions affect cell stability, attempting to make a safety assessment based solely on the cathode material does not tell the whole story** [2]. Cathodes of various types react destructively with electrolyte at temperatures between 130°C and 250°C.

Anode materials have been shown to react at much lower temperatures and, in general, lithium-ion cells are not rated for storage or use at temperatures above 60°C.

2.1.1 Physical or electrical abuse

Piercing a cell with an object that causes a short circuit between electrodes will create an uncontrolled current flow within the cell. This results in cell heating that itself drives increased ion flow, producing thermal runaway.

At the anode, lithiated carbon and electrolyte are not thermodynamically stable. During the manufacturing process this instability is handled by slow, controlled charge and discharge cycles that form a "solid electrolyte interphase" (SEI) layer on the anode surface [2], stabilizing the cell. Piercing the cell disrupts this SEI layer resulting in localized instability that produces heat.

Crushing or compressing battery modules can produce the same sort of internal damage as piercing, disruption of the SEI layer at the anode, as well as direct short-circuit of the anode and cathode.

Abusively overcharging a cell also causes cell heating. This precipitates anode-electrolyte reaction as well as internal short circuits, likely from separator failure [4], again producing conditions allowing thermal runaway.

2.1.2 Overheating

Overheating can occur for such reasons as electrically overloading a cell, environmental overheating, or fire, or overcharging. Electrode type, separator material, and behavior of the battery management system (BMS) are the key factors in how a cell reacts to overheating.

2.2 CHEMISTRY OF VERTIV'S BATTERY AND WHERE IT RATES COMPARED WITH OTHERS

Vertiv sources two types of Lithium-Ion battery modules:

Samsung SDI - Lithium Manganese Oxide / Lithium Nickel Cobalt Manganese Oxide comb (LMO/NMC). The Samsung cells are prismatic construction - flat, with aluminum shell on each cell; cells are arranged in a module case [5]. The electrolyte is liquid organic solvent. The product specification states abused cells may vent explosive gas [6].

Vertiv HPL - Lithium nickel manganese cobalt (NMC). Vertiv's cells are pouch style – flat envelopes that require mechanical protection provided by the module assembly case [7].

Vertiv lists the recommended operating temperature for the Samsung batteries as 23°C ± 5 and for the Vertiv HPL as 22°C - 30°C; both much less than conventional maximum recommended 60°C temperature for lithium-ion batteries.

2.2.1 History of problems with Vertiv's battery chemistry

Common search results for Samsung SDI battery failures are dominated by the issue with the Galaxy Note 7 cell phone. No recent reports were found related to larger battery assemblies.

There are no common search results for Vertiv HPL battery failures.

2.2.2 Off gas composition for Vertiv's battery

This author's research suggests battery assemblies sourced by Vertiv behave consistently with expectations for NMC cells regarding vented gas.

3. TYPES OF CONSTRUCTION

3.1 SEPARATORS

Maintaining physical separation between the anode and cathode is a key element in lithium-ion batteries for normal operation and for preventing internal short-circuit and resultant thermal runaway. Battery manufacturers use several methods.

3.1.1 Materials

Various hydrocarbon plastics are used as cell separators both individually and in combination with other polymers and coatings. Porous polyethylene (PE) appears under such product names as Teklon and Tonen [4], and in combination with polypropylene (PP) as Celgard.

Other polymers used include polyethylene terephthalate (PET) and polyvinylidene fluoride (PVdF) though these are much less common than PE and PP.

Ceramics are used in combination with supporting polymer films. Ceramics based on alumina, zirconia, and silica are layered with PE, PP, PET, or PVdF to yield separators with melting temperatures much greater than polymers alone. This characteristic improves cells' tolerance for physical abuse.

3.1.2 Shutdown

Multi-layer separators may be designed to inherently choke off current flow in the event of overheating. This is accomplished by using materials that melt at different temperatures. The inner layer melts sooner and fills the pores of the outer layers. This stops current flow through the cell thus reducing the energy contribution to thermal runaway. A shutdown separator can effectively prevent thermal runaway in electrically overloaded cells or in reaction to small, internal flaws.

Shutdown separators contribute to cell safety up to the melting temperature of their constituent materials. Typically above 150°C [2], the separator plastic melts, allowing an internal short-circuit that fully releases all cell energy. Such conditions generally arise where the battery assembly is engulfed in fire or has been pierced.

4. CODES AND STANDARDS THAT APPLY TO LI ESS

4.1 NFPA 855

NFPA 855 [8] is the Standard for Installation of Stationary Energy Storage Systems. The document covers capacitors, fuel cells, and batteries, with placeholders for super-conducting magnets and flywheels. Consistent with other NFPA standards, 855 focuses on the safe installation and operation of listed energy storage systems (ESS), and protection of personnel and surrounding facilities.

4.2 DOT 38.8

United Nations / Department of Transportation Manual of Tests and Criteria subsection 38.8 describes testing that lithium-ion batteries must pass in order to be considered safe for international shipping. The testing criteria parallel UL 1642 / 2054.

4.3 UL 1642 AND UL 2054

Abuse tolerance tests include over-discharge and short circuit; over-charge; crush, impact, shock, vibration; over-heating to 130°C and temperature cycling; low pressure. Batteries must survive without thermal runaway.

Samsung SDI batteries and Vertiv HPL batteries are UL 1642 compliant.

4.4 UL 1973

Fire propagation testing requires induced single cell failures prevented from propagating outside the enclosure. Assemblies are evaluated for cell manufacturing quality control, battery management systems, fire resistant cell and enclosure materials. Testing is conducted under normal use and abuse scenarios [9].

Samsung SDI batteries and Vertiv HPL batteries are UL 1973 compliant.

4.5 UL 9540A

The UL 9540A test method is four-tiered: testing at the cell level, testing at the module level, testing at the unit level, and testing in a final installation. Samsung SDI and Vertiv HPL battery assemblies are compliant at the Unit (Rack) level. This means that a thermal runaway condition may occur but, if it does, the fire does not propagate beyond the affected rack assembly. UL 9540A requires that if a thermal runaway occurs: the rack surface temperature is less than cell surface temperature that would cause venting (in nearby batteries), rack wall temperature remains less than 97°C, and there would be no explosion hazards and no flaming beyond the rack enclosure [10]. Compliance at the unit level also means that final installations do <u>not</u> require UL listing on a facility-by-facility basis.

Samsung SDI battery assemblies are UL 9540A compliant at the unit (rack) level.

Vertiv HPL batteries are UL 9540A compliant at the unit (rack) level with the local AHJ given discretion regarding 36-inch equipment separation.

5. SPECIFIC SAFETY FEATURES OF VERTIV LI BATTERY

5.1 BATTERY MANAGEMENT SYSTEMS

Battery management system (BMS) components are built-in to battery modules.

The Vertiv HPL BMS has a redundant internal power supply, fed from the battery, and reports an alarm on loss of redundancy. The BMS itself is redundant at the module level. The HPL rack level equipment can communicate Modbus/IP for reporting system status and alarms.

The Samsung SDI BMS has a redundant internal power supply, fed externally. The BMS is redundant at the System/Rack level.

6. SUPPLEMENTAL SAFETY FEATURES

6.1 SPECIAL TRAINING AND EQUIPMENT FOR FIRE DEPARTMENT PERSONNEL

Protection of First Responders will be guided by NFPA 855.

ESS fires have a Class C element because of the electrical components; however, the flammable/combustible materials also make ESS fires Class B.

As with all fires in modern structures where plastics are present, the toxic products of combustion in an ESS fire are a serious respiratory hazard to first responders.

Time Sequence Mapping of thermal runaway [11] has shown several distinct fire and smoke events that may occur during a lithium-ion battery fire: (1) venting and possible ignition of light electrolyte solvent, (2) venting and possible ignition/decomposition of heavier electrolyte including $LiPF_6$, and finally (3) destruction of the cell as thermal runaway consumes the internal components and may ignite the case. Actual time for this sequence is unpredictable and varies from total involvement in a few seconds to gradual consumption of individual cells across hours. First responders must be made aware that an ESS fire may initially appear limited but can evolve rapidly and unpredictably.

First responders must be provided instructions for how to quickly disconnect and isolate ESS components.

Uptime Institute recommends data centers employ Very Early Smoke Detection (VESDA), fire barriers and system separation, and water sprinkler or low-pressure clean agent systems [7, 12]. Routine maintenance to assure detection and suppression are in good operating condition is essential.

Concerns have been raised that the off-gas species which may arise during early battery venting will not be detected by VESDA or other conventional fire detection sensors. Products such as Nexceris Li-Ion Tamer (https://liiontamer.com/) offer rack level vent gas detection that can complement or integrate with rack level BMS equipment. Such a system, when interfaced with the BMS, can stop the charging current several minutes before an irreversible thermal runaway event can occur. This works if the failure is the result of overcharging and can at least contribute to an orderly shutdown in other circumstances. Situations beyond the scope of the Battery Management System such as severe ambient over temperature, mechanical damage, or catastrophic battery defects, will initiate alarms and trigger BMS shutdown; however, next level responses would be required. Off-gas monitors are typically configured to be redundant – separate from and independent of other systems that monitor and control battery charging.

6.2 SPECIAL SIGNAGE ON UPS

NFPA 855 4.3.5 identifies signage requirements for ESS battery rooms.

6.3 VENTILATION

NFPA 855 B5.3 and B5.4 do not call out ventilation requirements specific to lithium-ion or lithium metal batteries though the standard does generally refer to “ventilation”, “exhaust”, and “deflagration venting systems” in various paragraphs of Chapter 4. The facility’s Authority Having Jurisdiction will make the final determination on elements required for each installation.

6.4 SPRINKLER LOCATION

Sprinkler heads should be located according to criteria for fire suppression in electrical rooms. Selection of K-factor to yield fine mist for smoke reduction in the vicinity of ESS racks would be advisable.

REFERENCES

[1] D. Sturk, L. Hoffmann, and A. Ahlberg Tidblad, "Fire Tests on E-vehicle Battery Cells and Packs," (in eng), *Traffic Inj Prev,* vol. 16 Suppl 1, pp. S159-64, 2015, doi: 10.1080/15389588.2015.1015117.

[2] C. Mikolajczak, M. Kahn, K. White, and R. T. Long, "Phase 1 Final Report," in "Lithium-Ion Batteries Hazard and Use Assessment," The Fire Protection Research Foundation, 2011. [Online]. Available: https://www.nfpa.org/News-and-Research/Data-research-and-tools/Hazardous-Materials/Lithium-ion-batteries-hazard-and-use-assessment

[3] C. F. J. Francis, I. L. Kyratzis, and A. S. Best, "Lithium-Ion Battery Separators for Ionic-Liquid Electrolytes: A Review," *Advanced Materials,* https://doi.org/10.1002/adma.201904205 vol. 32, no. 18, p. 1904205, 2020/05/01 2020, doi: https://doi.org/10.1002/adma.201904205.

[4] C. J. Orendorff, "The Role of Separators in Lithium-Ion Cell Safety," *Interface magazine,* vol. 21, no. 2, pp. 61-65, 2012/01/01 2012, doi: 10.1149/2.f07122if.

[5] A. Beck, "LITHIUM BATTERIES: CYLINDRICAL VERSUS PRISMATIC," no. 05/26/2021. [Online]. Available: https://blog.epectec.com/lithium-batteries-cylindrical-versus-prismatic

[6] "Product Specification - Lithium Ion Battery System f or UPS U6A4," ed: Samsung.

[7] K. Araujo, "Prismatic Cell and Pouch Batteries - Lithium Ion Battery Applications," no. 05/26/2021. [Online]. Available: https://www.epectec.com/batteries/prismatic-pouch-packs.html

[8] *Standard for Installation of Stationary Energy Storage Systems*, N. F. P. Association, 2020. [Online]. Available: https://www.nfpa.org/codes-and-standards/all-codes-and-standards/list-of-codes-and-standards/detail?code=855

[9] L. Florence, "HOW SAFETY STANDARDS ADDRESS THE HAZARD OF FIRE PROPAGATION IN BATTERY SYSTEMS," presented at the Safety Forum, Sandia National Lab, 2017. [Online]. Available: https://www.sandia.gov/ess-ssl/docs/conferences/safety_forum_2017/presentations/Day_2_Application_to_Scale_3/4_Florence_AS_3.pdf.

[10] "UL 9540A Battery Energy Storage System (ESS) Test Method." UL. https://www.ul.com/news/ul-9540a-battery-energy-storage-system-ess-test-method (accessed 06/01/2021, 2021).

[11] X. Feng *et al.*, "Time Sequence Map for Interpreting the Thermal Runaway Mechanism of Lithium-Ion Batteries With LiNixCoyMnzO2 Cathode," (in English), *Frontiers in Energy Research,* Original Research vol. 6, no. 126, 2018-November-26 2018, doi: 10.3389/fenrg.2018.00126.

[12] A. Lawrence, "Datacenter Fire Frequency." [Online]. Available: https://journal.uptimeinstitute.com/datacenter-fire-frequency