Energy Storage System Safety:

Comparing Vanadium Redox Flow and Lithium-Ion Based Systems

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"The flammable gases generated from (Li-ion) batteries are the main source of explosion risk".

- DNV-GL/ConEd Report




Introduction

The nascent field of large format stationary energy storage systems (ESS) is expected to experience significant growth in all sectors of the US power grid, from residential to utility installations. The specific technology and chemistry selected for a particular project takes into account many factors with safety taking a higher priority for many of these design decisions. The knowledge base of some ESS chemistries is also at an early stage in its development of installation codes, standards, and regulations (CSR).

The potential risks in early adoption of new technologies includes:

(1) An immature regulatory landscape that may impose more stringent requirements than necessary out of an abundance of caution.
(2) Imposing less stringent requirements than prudent, based on misconceptions of the inherent dangers of the underlying technologies.
(3) Withholding any approvals until specific requirements and sufficient documentation on safety exist.

This paper will compare, at a high level, the safety considerations for lithium ion batteries and vanadium redox flow batteries and how the systems function and behave; it will also review the relevant standards for these technologies.

As of 2017, the current state of operational stationary ESS installations consists primarily of commercial and utility scale systems, both in front of and behind the meter.

Drivers for the wide deployment of ESS include both cost reduction and operational resiliency as well as additional grid services including, but not limited to:

- Local and statewide energy storage incentives and mandates.
- Reducing demand charges.
- Load shifting for time-of-use savings or arbitrage.
- Grid support services such as frequency regulation and ramping needs.
- Smoothing or buffering of intermittent renewable resources (PV or wind).
- Back-up of electrical loads in the event of outages.

ESS Types

Table 1: Common ESS Types

	Common types of ESS
Pumped Hydro	Water is pumped from a lower elevation source during periods with reduced electric rates to a higher elevation for storage and used to spin generators at higher electric rate periods.
Mechanical	Compressed air energy storage (CAES) pumps air into caverns or tanks at high pressures and releases it to spin generators. Flywheels utilize kinetic energy in large mass cylinders spinning at high RPMs in a vacuum. When power is needed, a motor engages to generate electricity as the wheel spins down.
Thermal	Solar radiation is focused on a heat transfer medium, which can be used to generate steam to spin generators for electrical energy production. This heat can also be stored in oils or other fluids, or as molten salt, for use when solar radiation is not available.
Electro-chemical	Electrical energy is stored via chemical bonds or via reversible chemical processes require an electrolyte and electrodes (cathode and anode)

Electrochemical Energy Storage

Though pumped hydro, based on storage volume of reservoirs and dams, still comprises the bulk of energy storage in the US, electrochemical energy storage is growing rapidly and poses more unique threats of greater consequence and likelihood than does elevated water.

Fire safety and prevention personnel should take special note of these technologies, as they are among the most rapidly declining in cost, technically mature, and are more widespread and are rapidly entering markets across the country.

Within the family of electrochemical batteries, there are several sub-types each with their own chemistries and fire protection needs. This paper will introduce this family of ESS, then provide further insight into the two most prevalent technologies – lithium-ion and flow batteries:

Lithium Ion:

$LiCoO_2$ - Lithium Cobalt Oxide
$LiMn_2O_4$ - Lithium Manganese Oxide
$LiNO_2$ - Lithium Nitrogen Oxide
$LiAlO_2$ - Lithium Aluminum Oxide

These chemistries are mainly used in consumer products, like cell phones, laptops, hover boards, etc.

$LiTiO_3$ - Lithium Titanate ("L-Titanate")
$LiFePO_4$ - Lithium Iron Phosphate ("LFP")
$LiNiMnCoO_2$ - Lithium Nickel Manganese Cobalt ("NMC")
$LiNiCoAlO_2$ - Lithium Nickel Cobalt Aluminum ("NCA")

These chemistries are most common in mobile transportation (EV's) and stationary ESS.

Other Traditional Technologies: Lead-acid (flooded and AGM), Nickel-metal hydride, Nickel-iron.

Sodium Beta: Sodium sulfur most common

Flow Batteries: Vanadium redox, Zinc-Bromine, Iron-Chromium, Iron-Iron

Hazards

There have been concerns expressed from several groups of stakeholders— property owners, insurance underwriters, fire service, and building code officials— regarding the risk of overheating, flammable and toxic gas production, thermal runaway, leakage of hazardous materials, and stranded energy in damaged batteries.

The ESS field includes a variety of technologies, each with a range of potential hazards from corrosive spill hazard to explosion. The types of ESS and their sub-families, are important to understand so that the specific hazards can be better mitigated.

Table 2: Typical Hazards by ESS Type

Risk	Lithium-ion	Flooded Cell	Sodium Sulfur	VRB Flow Battery
Voltage	X	X	X	
Arc-Flash/Blast	X	X	X	
Toxicity	X	X	X	X
Fire	X	X	X	
Deflagration	X	X		
Stranded Energy	X	X	X	

Electrical Shock/Arc Flash

Electrical shock presents a risk to workers and responders as most ESS cannot be "turned off", with the exception of some flow batteries. Damaged batteries represent the potential for a significant hazard due to the inability to safely discharge the stored energy in the damaged cells. This is referred to as "stranded energy," and presents unique mitigation hazards. Arc flash or blast is possible for systems operating above 100V. Most lead-acid ESS in telecom settings operates at below 60V, yet there exists the potential for high fault currents present in the case of a short circuit even at these relatively lower voltages. Limited safe operating space may place personnel within the range of burn injuries. Li-ion systems operate from 48Vdc – 1000Vdc depending on the battery design. Currently there are limited inverter options suitable for higher voltage, but even now higher voltage systems are planned and will likely be coming online in the coming years.

Flow batteries do not have the same short circuit fault current potential present, and therefore do not present as great a shock or arc-flash hazard when the system is off. This will be discussed in more detail in the Flow Battery section.

Toxicity/Corrosiveness

Toxicity or corrosion risks may be present in aqueous electrolyte or from off-gassing produced by over-heating aqueous or vaporized electrolytes. In addition, lithium ion batteries and flow batteries in fire scenarios may generate toxic gas from the combustion of hydrocarbons, plastics, or acidic electrolytes.

Fire/Deflagration

Fire hazards may be present from either aqueous or vaporized electrolyte. Charging aqueous batteries (including flooded lead acid and AGM can electrolyze water into hydrogen and oxygen. Battery systems with this hazard are required to be equipped with exhaust & H_2 detection systems.

When li-ion cells are exposed to temperatures over 80C (176F), they can generate heat at a faster rate than they are able to dissipate it, presenting a thermal runaway risk. This can occur from a variety of abuse modes including thermal abuse, mechanical abuse, or manufacturing defects. Thermal runaway fires can produce temperatures above 2000 F while forcefully venting vaporized flammable and toxic electrolyte gases. Gas or aerosol based fire suppression systems in Li-ion battery systems are not recommended as they are not believed to be effective at stopping either the thermal runaway process or complete combustion; as cooling – not oxygen reduction – is required to stop the thermal runaway or combustion process. Deflagration hazards may be present in confined or enclosed spaces when flammable gasses, which are produced in great quantities, reach both the explosive range and auto-ignition temperatures, especially since ignition sources also exist due to the electrical nature of the components. Because of the dense configuration of many li-ion cells within modules, prevention of thermal runaway is critical and is one of the primary functions of a battery management system.

Ventilation, Exhaust and Deflagration Venting and Protection

One of the primary concerns with Li-ion ESS installed inside structures is the generation of flammable gasses created during thermal runaway and cell venting. Depending on the quantity of cells that enter runaway and the cause and conditions, the volume and type of gasses created can vary widely. Burn tests have identified many flammable gasses produced during overheating such as carbon monoxide, hydrogen fluoride, hydrogen chloride, methane, ethane, ethylene, and propylene. Depending on the rate of heating, gas production can be quite rapid and may vent from the cell with significant pressure. In fact, the rate of gas release could exceed the design capacity of the exhaust system.

In the DNV-GL/ConEdison testing, a recommendation was made for ventilation, based on the production of HCL found in all battery types tested:

> *"…it should be noted that in the smallest unit of failure scenarios, the recommended ventilation rate of 0.25 ACH is well below the typical rating of 3-4 for most general spaces which means that vanadium redox and Pb (lead) acid batteries, as well as single cell failure modes for Li-ion, are already within the implied code requirements " DNV-GL Report*[1]

Note that the recommendation assumes a single cell failure mode in Li-ion systems. This may not be an adequate failure assumption to address more significant failures with this technology where there could be thousands of cells wired together within modules making up numerous batteries in close proximity. This concern is particularly prudent for ESS installed inside occupied structures.

[1] Considerations for ESS Fire Safety, DNV-GL/ConEdison, Jan 18, 2017

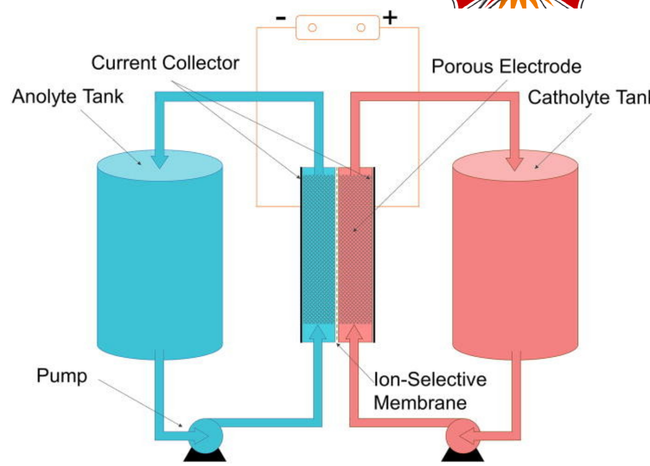
Fire Suppression

The need for engineered fire suppression systems is a challenging issue for fire protection engineers as current fire codes provide little in the way of recommendations. As a result, some are taking a proactive approach in the early stages based on limited available test data. Early large-scale fire tests with Li-ion ESS have shown that cooling of the cells during suppression is critical to terminating the production of flammable combustion gasses. The density of Li-ion cell configurations in large scale ESS, as well as the various cabinet configurations currently found in installed systems, make active cooling with water more complex. An installation sited in an existing building equipped with a NFPA 13 fire sprinkler system may still not allow the water to contact modules containing cells on fire. The DNV GL report cites testing in which aerosolized suppression system activation suppressed visible flame, yet had no effect on cell burning and combustion gas production. In fact, this condition could lead to an explosion as responders gain entry to the container, thereby allowing oxygen to bring the gas mixture into the explosive range. Included in their report are recommendations to include a cascading response where suppression systems may include a gas phase agent for initial discharge and deploy water if heat buildup continues.

More testing is needed on optimal suppression system design and placement to provide early system fire protection with indoor Li-ion ESS installations. The NFPA's Fire Protection Research Foundation along with FM, has completed three phases of research into managing Li-ion battery hazards as a commodity.[2] This has generated some data for sprinkler design but primarily for Li-ion stored as a commodity and not operational ESS.

2. http://www.nfpa.org/news-and-research/fire-statistics-and-reports/research-reports/hazardous-materials/lithium-ion-batteries-hazard-and-use-assessment

Flow Batteries



Flow batteries are based on two aqueous electrolytes serving as either the anolyte or catholyte with different charges that are pumped from separate storage tanks across a membrane in a fuel cell. Power is only produced when the pumps and control systems are operating, and as such there is no risk from "stranded energy" as with other electrochemical batteries.

The chosen electrolyte is based on the system design. This paper will address only Vanadium Redox as it is currently considered one of the safest flow battery technologies currently available. This is supported by operational and test data available from 20+ years of systems installed in various different applications, environmental conditions, and product configurations world-wide.

Vanadium Redox flow battery (VRB) systems do not represent the same fire or deflagration risk as Li-ion based ESS for several reasons. First, the aqueous electrolyte is not flammable. Secondly, any deviation from safe operating parameters will trigger the shutdown of system pumps, ceasing to charge the electrolyte, thus reducing the chance of accidental H2 generation. Additionally, the thermal mass of the electrolyte tanks can provide an additional barrier to overcharging conditions by allowing ambient temperatures during overnight discharge times to cool the VRB for the next charge cycle. In any case, H2 production is a common condition easily managed in all lead-acid ESS systems and better understood by fire protection engineers in the system design and commissioning if installed indoors.

While not flammable, the electrolyte in VRB systems is corrosive. It is comprised of a sulfuric-acid based solution similar to common automotive lead-acid batteries. While very similar to lead-acid batteries, VRBs are notably different and deemed safer than lead-acid for the following reasons:

(1) Unlike traditional lead-acid batteries, VRBs do not include lead. Therefore, VRBs do not have the toxicity issues of lead that conventional car batteries do. The only potential source of toxicity in a VRB is when Vanadium is in powder form, but when mixed into liquid form in the final product and put into operation, the VRB is deemed non-toxic due to the very low concentration levels of Vanadium.

Some VRB batteries may also include hydrochloric acid, but will still be at a similar pH.

(2) VRB has a lower concentration of sulfuric acid further than traditional lead-acid batteries. By comparison, VRB electrolyte is 15% vanadium, 25% sulfuric acid, 60% water (by volume), whereas lead-acid is 25% lead, 25% sulfuric acid, and 50% water (by volume). Systems with HCl will maintain a similar or slightly higher balance of acid, but will operate at a similar pH.

Leaks must be expected in any hazardous fluid handling equipment. Secondary containment is typically designed into the system and standard corrosive PPE is required for liquid handling. Reliability of leak detection and annunciation is paramount. One manufacturer has addressed the reliability issues of sensors by placing the pump intake at a high level in the tank. A very small reduction in tank volume results in the pump running dry. This is identified by motor controllers as a possible system leak and pumps are rapidly shut down.

In the area of shock hazard, voltage is produced in a flow battery only when electrolytes are present in a cell stack. If one turns off the motors and fluids drain from the cell stack, then the cell stacks have no measurable voltage at the terminals. This happens not only when the battery is forcibly "turned off," but also in "standby mode," which the battery enters when it's not actively providing some sort of charge / discharge event. This safety characteristic is unique to Vanadium flow batteries. All other batteries maintain a charge and potential shock hazard depending on the voltage. Even Zinc-Bromine flow batteries don't have this characteristic because those batteries still include a metal plate that holds a charge, presenting a shock hazard. Vanadium flow batteries are the only "all-aqueous" flow battery since they don't include any metal plates to hold the chemical reactions / charges / voltages.

Vanadium flow batteries are also unique in terms of short circuit fault current potential, because:

(1) The internal dynamics of the battery are such that the energy discharge is limited to the fluid in the battery at any given time’ typically this is less than 1% of total stored energy.
(2) Vanadium flow batteries have been tested under dead-short conditions resulting in normal system operation, with no danger to either equipment or personnel.

Currently flow batteries are found only in commercial, industrial, and utility-scale applications, however manufacturers are expected to introduce residential flow battery systems in the future. While its efficiency and energy density are lower than lithium-ion, flow batteries compensate with longer life and safety features that enable lower fire protection requirements.

Codes, Standards, & Regulations

Commonly grouped together and referred to as CSR, Codes and regulations typically dictate how a product is installed, while product standards dictate the tests a product must pass to receive a certification or listing as being safe when used per manufacturer's instructions.

Codes such as building, fire, or electrical codes are typically updated on a 3-year cycle and are adopted on often different schedules at the federal, state, local, tribal and territorial level as well as by utilities, insurance interests and other non-regulatory bodies.

Product standards are updated as needed based on either change in building codes or identified safety requirements.

The applicable published building, fire & electrical codes including chapter relating to ESS include:

2015 International Fire Code	Chapter 12
2015 International Residential Code	Chapter R327
2015 NFPA1 Fire Code	Chapter 52
2017 National Electric Code	Article 706

The NFPA has created a new standard for ESS, "NFPA 855: Standard for Installation of Stationary Energy Storage Systems" which is expected to be published in late 2018 to address the design, installation, and commissioning of ESS. This standard will likely be referenced by the NEC and both Fire Codes as a key document.

UL STANDARDS

The primary applicable US standards relating to ESS include:

UL 1642 (Lithium Batteries)

UL 1973 (Batteries for Use in Light Electric Rail and Stationary Applications)

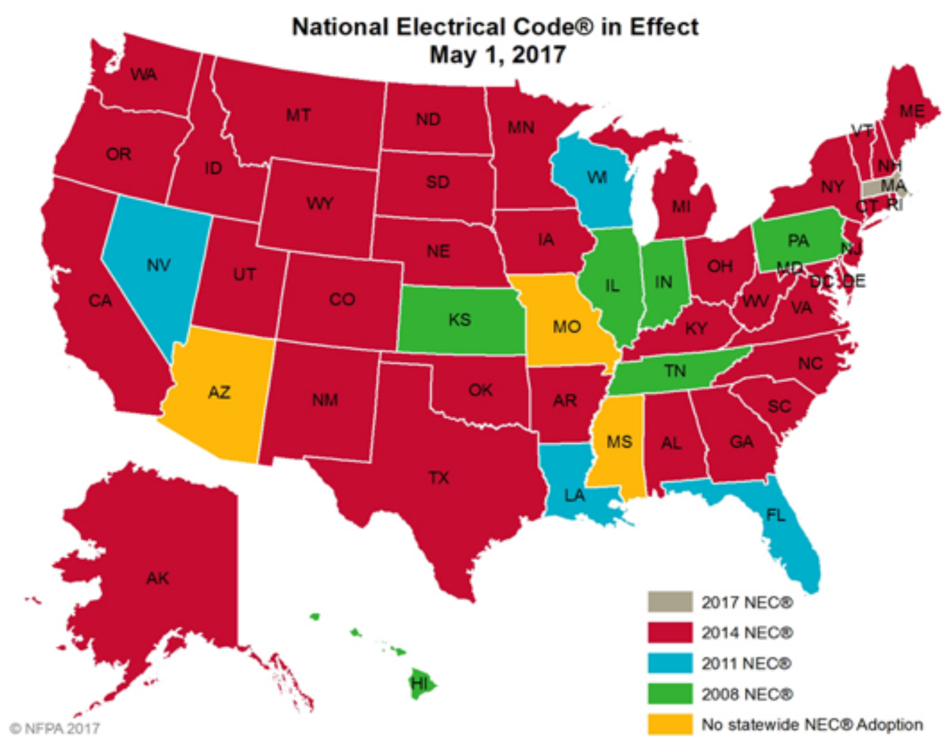
UL 1741 (Inverters and Power Electronics)

UL 9540 (Energy Storage Systems)

National Electric Code

Installation requirements for ESS are covered in the National Electric Code (NEC). The 2017 NEC includes a new article 706 “Energy Storage Systems” for the 2017 cycle. It covers classification of systems, requirements for disconnect locations and marking, over-current protection, ventilation, and their listing requirements.

All ESS systems will need to be listed to safety standards such as UL 9540 to address the batteries, inverters, and battery management systems. The system classification identifies whether the system is pre-engineered and comprised of listed components, or listed as a self-contained system. Adoption of the NEC is typically by state and the chart below shows the current cycle in each state as of May 2017.



ESS Installed in locations currently on the 2014 NEC (or earlier) have less guidance with only article 480 "Storage Batteries" available for reference. There is very little code language on safe installation practices for lithium-ion storage systems prior to the 2017 NEC.

Fire Codes

Fire Codes are being updated to address ESS beginning in the 2018 cycle of both the International Fire Code (IFC) and NFPA1 Fire Code. Technical committees are trying to ensure that both codes are harmonized to the maximum extent possible in order to avoid conflicting recommendations. The IFC section on ESS in Chapter 12 will address the following:

- Threshold quantities for various chemistries
- Listing of systems to UL 9540
- Requirement for Hazard Mitigation Analysis or Failure Modes Effects Analysis (FMEA) related to fire safety
- Location & Separation of battery systems
- Maximum allowable quantities and sizes requiring permitting based upon kWh instead of electrolyte quantities

In both the 2018 Fire Codes and the draft of NFPA 855, lithium-ion technologies will likely see more stringent requirements in terms of fire suppression systems and exhaust and/or deflagration venting. Early testing, such as DNV-GL/ConEdison's research cited above, recommended allowances for reduced fire suppression systems in ESS with non-flammable electrolyte. For all others, water-based sprinklers were proposed for any ESS with a flammable electrolyte when installed indoors.

> *"If a battery is demonstrated to have a non-flammable electrolyte, there may be considerations for a reduced water extinguisher requirement, or at a minimum a water requirement equivalent to that required for the space without battery systems installed.*
>
> *The ventilation requirements should be the same for all battery chemistries tested in this program because they all have varying degrees of HCl or similar toxic emission upon heating."*[3]

3. Considerations for ESS Fire Safety, DNV-GL/ConEdison, Jan 18, 2017

Written into the Fire Codes are exceptions for large scale fire testing. Key to this will be a standardized test protocol that produces repeatable results that can be used to determine safe clearances to ensure that a fire in a battery remains contained and does not extend to unaffected units, or the structure. Flow battery systems will only require exhaust if installed inside structures. As of the writing of this paper, UL is expected to release an outline of investigation covering full scale testing.

Summary

Vanadium flow battery systems offer significant safety advantages relative to li-ion in the areas of short-circuit fault, arc-flash / blast, “stranded” energy, fire suppression, and deflagration. This can lead to a streamlined review and approval process for all stakeholders involved.

When comparing available ESS technologies, many factors will affect the final system choice. From a safety perspective, significant questions remain unanswered when it comes to protecting Li-ion batteries from thermal runaway, even more so in an occupied structure. If codes continue developing along their current trajectory, many structures may not be suitable without significant modifications. As one designer of naval-based ESS explained, “A submarine must have a significantly higher level of safety than a land based structure, as escape is impossible”. However, when looking at ESS installations inside high-rise apartment dwellings, these structures may be compared to submarines standing on end in terms of life hazard profiles.

This highlights the need for AHJ’s to adopt current CSR, or “look forward” to published but not yet adopted codes to assist in the safe installation of ESS.

Author Biography

Fire Captain Matthew Paiss is a 21-year veteran of the San Jose Fire Department. He is the IAFF primary representative to NFPA 70 (NEC) and NFPA 855 Energy Storage Systems standards. He is a subject matter expert for the National Fire Protection Association on energy storage, and President of Energy Response Solutions, Inc. (a training and consultation firm). He has contributed to the IFC & NFPA1 fire code sections on PV & ESS. CA Paiss has delivered PV & ESS Safety training to over 7000 firefighters across N. America including the FDIC and the National Fire Academy. He has spoken in Europe on fire safety and PV design and holds certificates as a credentialed California Technical Education Teacher, Registered State Fire Instructor, and Certified State Fire Officer.

He is a member of UL Standards Technical Panels 1703 & 1741, and has written for Fire Engineering, SolarPro and SFPE magazines.

About Energy Response Solutions, Inc.

Energy Response Solutions, Inc. provides electrical safety training development & delivery for the fire service community, fire and electrical safety codes & standards consultation to alternative energy system designers, integrators, and Authorities Having Jurisdiction (AHJ).