ACS Energy Letters

http://pubs.acs.org/journal/aelccp

Battery Hazards for Large Energy Storage Systems

Cite This: *ACS Energy Lett.* 2022, 7, 2725−2733

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

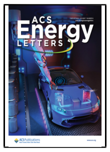
Energy storage systems (ESSs) offer a practical solution to store energy harnessed from renewable energy sources and provide a cleaner alternative to fossil fuels for power generation by releasing it when required, as electricity. The energy stored and later supplied by ESSs can greatly benefit the energy industry during regular operation and more so during power outages. Electrochemical energy storage has taken a big leap in adoption compared to other ESSs such as mechanical (e.g., flywheel), electrical (e.g., supercapacitor, superconducting magnetic storage), thermal (e.g., latent phase change material), and chemical (e.g., fuel cells) types, thanks to the success of rechargeable batteries. Figure 1 depicts the various components that go into building a battery energy storage system (BESS) that can be a standalone ESS or can also use harvested energy from renewable energy sources for charging. The electrochemical cell is the fundamental component in creating a BESS. A module is a set of single cells connected in parallel-series configurations to provide the required battery capacity and voltage. The complete set of modules arranged in racks constitutes a battery. A battery management system (BMS) allows for monitoring and controlling the charge and discharge of the battery. Thermal management of the battery is managed by the heating, ventilation, and air conditioning (HVAC) system that controls the environmental temperature and humidity. Integrating the BESS with renewable energy sources for the charging process can be done directly or through an AC/DC inverter. The BESS battery operates with DC, and renewable energy sources can produce both AC and/or DC current. The DC/AC inverter also enables the BESS to be integrated with the electrical grid by demanding energy when needed or supplying excess energy, as long as the minimum requirements of the grid are met.

Battery technologies currently utilized in grid-scale ESSs are lithium-ion (Li-ion), lead−acid, nickel−metal hydride (Ni-MH), nickel−cadmium (Ni-Cd), sodium−sulfur (Na-S), sodium−nickel chloride (Na-NiCl$_2$), and flow batteries.[1−3] Recently, some demonstration zinc−air systems have also been announced.[1,4] The main characteristics of these battery types are listed in Table 1. According to the data collected by the United States Department of Energy (DOE), in the past 20 years, the most popular battery technologies in terms of installed or planned capacity in grid applications are flow batteries, sodium-based batteries, and Li-ion batteries, accounting for more than 80% of the battery energy storage capacity.[1]

Li-ion batteries have become popular in new grid-level installations due to their rapidly decreasing prices and wide availability in the market. Large ESSs are manufactured with a variety of Li-ion chemistries, from those with a lithium iron phosphate (LFP) cathode to those with a nickel manganese cobalt oxide (NMC) cathode and with graphite, silicon composite, or lithium titanate (LTO) anodes.[1,6] Moreover, the second-life use of aged Li-ion batteries from electric vehicles in less demanding stationary applications has become a feasible concept to extend the useful life of those batteries. However, the economic viability of Li-ion battery reuse needs to be solved, and challenges regarding the safety of aged batteries, state-of-health determination, and compatibility issues need to be overcome.[6,7] Other battery technologies, such as lithium−sulfur, sodium-ion, and magnesium-ion types, are suitable for future use in grid applications due to their high energy density. However, these systems are still in the developmental stage and currently suffer from poor cycle life, preventing their use in grid energy storage applications.

Flow batteries store energy in electrolyte solutions which contain two redox couples pumped through the battery cell stack. Many different redox couples can be used, such as V/V, V/Br$_2$, Zn/Br$_2$, S/Br$_2$, Ce/Zn, Fe/Cr, and Pb/Pb, which affect the performance metrics of the batteries.[1,3] The vanadium and Zn/Br$_2$ redox flow batteries are the most commonly used and are already mature for grid-level applications. The advantages of flow batteries include lower cost, high cycle life, design flexibility, and tolerance to deep discharges. Additionally, high heat capacity is also effective in limiting high temperature rises in flow battery systems, making them safer systems compared to other rechargeable battery systems. The nature of the various compounds generated in flow batteries of various chemistries during charge and discharge has been characterized, but their behavior under off-nominal conditions, such as over-charge, over-discharge, and external short circuits, has not been characterized. System-level studies at large scale will shed light on the susceptibility of flow batteries to undergo

Received: June 18, 2022
Accepted: July 12, 2022
Published: July 25, 2022



ACS Publications

https://doi.org/10.1021/acsenergylett.2c01400

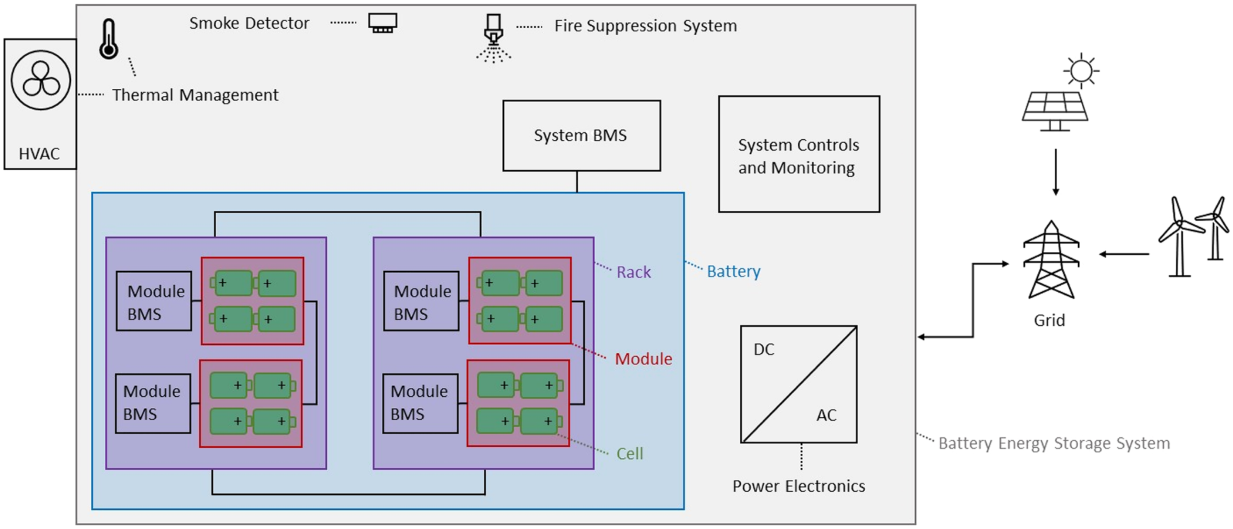


Figure 1. Depiction of a BESS that can be stand-alone or can get the energy to charge from other renewable energy sources.

Table 1. Key Properties of Common Battery Technologies Used in Grid-Scale ESSs[2,3,5]

property	Li-ion	flow	Na-S	Na-NiCl$_2$	lead–acid	Ni-Cd	Ni-MH	Zn-air
specific energy (Wh/kg)	100–240	10–85	150–240	100–120	30–50	50–75	40–110	110–650
specific power (W/kg)	500–2000	45–166	150–240	150–200	180–200	150–300	200–1200	100
nominal cell voltage (V)	3.6–3.8	1.2–1.9	2	2.6	2	1.2	1.2	1.4
energy efficiency (%)	>98	>75	75–90	90	75–85	70–85	60–80	50–65
cycle life	1000–10000	6000–14000	>2500	>2500	500–1000	2000–2500	300–2000	100–300

catastrophic failures resulting from off-nominal conditions during field usage.

The Na-S battery, in turn, is considered one of the most promising candidates for large-scale applications due to the desirable properties listed in Table 1. It has a working temperature of 300–350 °C, which is its main drawback, as it requires a heat source, and the highly exothermic reaction between molten Na and S increases the risk of fire.[3] The Na-NiCl$_2$ battery is a similar high-temperature system, originally developed to solve some of the problems of the Na-S system.[2] The other battery types, including lead–acid, Ni-MH, Ni-Cd, and Zn-air, make up a small percentage of the grid-level batteries.

The reactive and hazardous nature of Li-ion batteries under off-nominal conditions can lead to safety incidents and may cause extensive damage to the BESS. Table S1 lists reported failure incidents involving BESS installations worldwide since 2011.[8] The alarming rate of BESS failures in South Korea from 2018 to 2019 prompted a formal government investigation and a partial suspension of the country's energy storage facilities.[9] Failure of the protection systems to function during electrical surges led to explosions in some cases. The operational environment may have been prone to temperature fluctuations, moisture, and dust accumulation that led to accelerated degradation of components. Errors during installation of the ESS were also cited as probable causes. Additionally, a lack of an overall control and protective system for the ESS may have contributed to failures in some incidents.[9,10] The investigation also found manufacturing defects in the batteries, but the defective batteries were not implicated in the ESS failures due to lack of fire during verification tests on such batteries.[9] Subsequent investigation following additional ESS fires in South Korea led to different conclusions about the causes of failures. Faulty batteries prone to overheating were described as the cause of ESS fires, although this claim was debated by the battery manufacturers.[11] The fire and explosion incident at the Arizona Public Service (APS) McMicken Energy Storage Unit facility in 2019, that caused severe injuries to firefighters, was investigated by different entities and led to different conclusions on the source of initial thermal runaway. An investigation commissioned by APS claimed the source of initial thermal runaway to be internal short circuit due to abnormal dendritic growth within a single cell, whereas the investigation commissioned by the battery manufacturer claimed the source of initial thermal runaway to be external arcing at the battery level.[12]

Hazards Associated with Lithium-Ion Batteries. Hazards for Li-ion batteries can vary with the size and volume of the battery, since the tolerance of a single cell to a set of off-nominal conditions does not translate to a tolerance of the larger battery system to the same conditions. Li-ion batteries are prone to overheating, swelling, electrolyte leakage venting, fires, smoke, and explosions in worst-case scenarios involving thermal runaway. Failures associated with Li-ion batteries are described to be deflagration in nature. However, the gases produced as a result of a fire, smoke, and/or thermal runaway can accumulate to a combustible level in the installation location and cause an explosion (detonation). In general, the off-nominal conditions that can cause the occurrence of catastrophic events with Li-ion batteries can be categorized into electrical, mechanical, and environmental types. The most common electrical hazards are over-charge, over-discharge, and external and internal short circuits. Of the environmental hazards, off-nominal conditions such as temperatures beyond the manufacturer's recommended range are those that are well understood. The influence of other environmental hazard causes, such as changes in altitudes, pressures, salt fog, floods, rain, etc., are not as well understood. Mechanical hazards such as those caused by vibration, shock, and impact are understood to a certain level, especially those encountered under transportation conditions.

Electrical Hazards. Over-charge of Li-ion cells and batteries can occur when they are charged at a very high rate or to a voltage that is above the manufacturer's recommended specifications and limits for charging current are not appropriately designed into the system. Cathode destabilization,[13] lithium dendrite formation,[14] electrolyte decomposition, and the heat produced due to the high voltage or high charge rate can lead to catastrophic events. In addition, as cells and batteries age with storage and use, the individual cell's electrochemical characteristics change, such as capacity and internal resistance, and in a battery configuration this causes deviations in characteristics between the cells in the battery. The deviations grow larger if no balancing of the cells/cell banks is provided, leading to excursions of voltage beyond safe limits, thus resulting in a catastrophic failure.

Studies have shown that a cell's tolerance to an off-nominal condition such as an over-charge need not necessarily translate to a module- or battery-level tolerance to that same condition.[15] With the pouch format cells, due to the lack of internal protective devices like the current interrupt device (CID), the single cells go into thermal runaway with a fire and smoke when over-charged at medium rates such as 1 and 0.5 C.[16] It was also observed in the referenced study that pouch format cells were tolerant to a 0.3 C rate of over-charge current, but the same equivalent over-charge current caused cells in multicell series and/or parallel configurations to go into complete thermal runaway and fire.

An important factor to note for safe operation of batteries is the safety related to the use of appropriate chargers. Li-ion batteries have several types of metal oxides cathodes with a few different anode chemistries. In addition to the various combinations that can be obtained with the cathodes and anodes, electrolyte combinations can vary widely depending on the application load, cycle life and calendar life, and thermal and pressure environments. The chargers used should therefore be designed to accommodate the appropriate combination of electrodes and electrolyte. Traditionally, dedicated commercial chargers for low-energy applications of less than 60 Wh show a charge profile wherein the charge current starts falling even before the end-of-charge voltage (EOCV) is reached, as this helps to keep the temperatures low at the end of charge and also provides a margin for safety with respect to an over-voltage condition, which can be avoided with the gradual drop in charge current.[17,18] With large ESSs, all these factors need to be taken into consideration to prevent hazardous events due to an off-nominal over-charge/over-voltage condition.

Over-discharge is a process wherein the Li-ion cell is discharged below the manufacturer's recommended end-of-discharge voltage. In a single cell, one cannot discharge the cell below 0 V; however, when one considers a module or battery design, it is possible to take any one cell into an "over-discharge into reversal" condition where the voltage of the cell/cells is driven into negative voltages and energy is still being extracted, leading to undesirable electrochemical changes in the cell. This can occur, as with a large ESS, when there is an imbalance in the cell's electrochemical properties, such as capacity and internal resistance, described in simple terms as the "weak cell/cells".

At voltages below the manufacturer's recommended end-of-discharge value, dissolution of the copper current collector is initiated, and decomposition of electrolyte occurs. Under an extreme over-discharge condition, the dissolved copper ions deposit on the cathode, anode, and separator, and ultimately the system becomes an electrical wire instead of an electrochemical system, leading to a benign short circuit, making the cell or battery unusable. Subtle over-discharges, however, can lead to a catastrophic hazard without warning.[19] The bigger concern is the metallization of the dissolved copper ions and deposition of the metallic copper on the cathode, anode, and separator during the subsequent charge step.[19−22] This can lead to heating of the cell due to the effort that is required for the intercalation of lithium ions into the anode that has uneven copper deposition. At a certain point, lithium dendrites start forming on the surface of the copper layer, as the intercalation sites are covered with copper. This type of effect is more pronounced and can lead to a catastrophic thermal runaway in modules compared to that observed in single-cell batteries. In the absence of cell balancing in modules, a single or multiple over-discharges during the battery usage phase can lead to conditions in successive cycles that can subsequently lead to a catastrophic thermal runaway. The number of over-discharges that will lead to a catastrophic event depends on the extent of imbalance and over-discharge in the module.[23] With large ESSs, due to the significantly large number of cells required to build the battery system, cell-level voltage monitoring, cell balancing, and under-voltage cutoff at the module and battery pack levels are imperative.

External short circuit can be considered an electrical shock to the cell or battery. External short circuits can be high impedance or low impedance in nature. While the former occurs due to the lack of proper design to minimize the risk, the latter is more commonly observed and well known. Low-impedance or hard short circuits occur when the load imposed on a battery has a resistance that is equal to or less than the internal resistance of the article.

The occurrence of high-impedance shorts can be reduced by designing the battery pack in an appropriate manner with the inclusion of electrical insulation materials between and around the cells, anodizing the battery container, and confirming that the wires are rated appropriately for the currents they need to conduct, that there are no sharp corners, that the wires are not bent in a way that would cause breakage, that the design is not conducive to chafing of the cables and wires, and that any exposed metal tabs and surfaces are well insulated. Low-impedance short circuits can be protected with the use of hard-blow and resettable fuses, poly switches, and thermal fuses. If fuses are used, then the reaction time of the fuse should be such that it protects the battery before any cell-level internal protective devices, such as the positive temperature coefficient (PTC), get activated, especially when the battery is a high-voltage/high-capacity type. When two fuses are used, then the rating of the two fuses should be different to ensure two-failure tolerance and should take into consideration the loads that will be encountered in the application in order to prevent a nuisance trip.

Protection against external short circuits has been incorporated into cell designs in various forms. The PTC was one of the earliest innovations that was included inside the

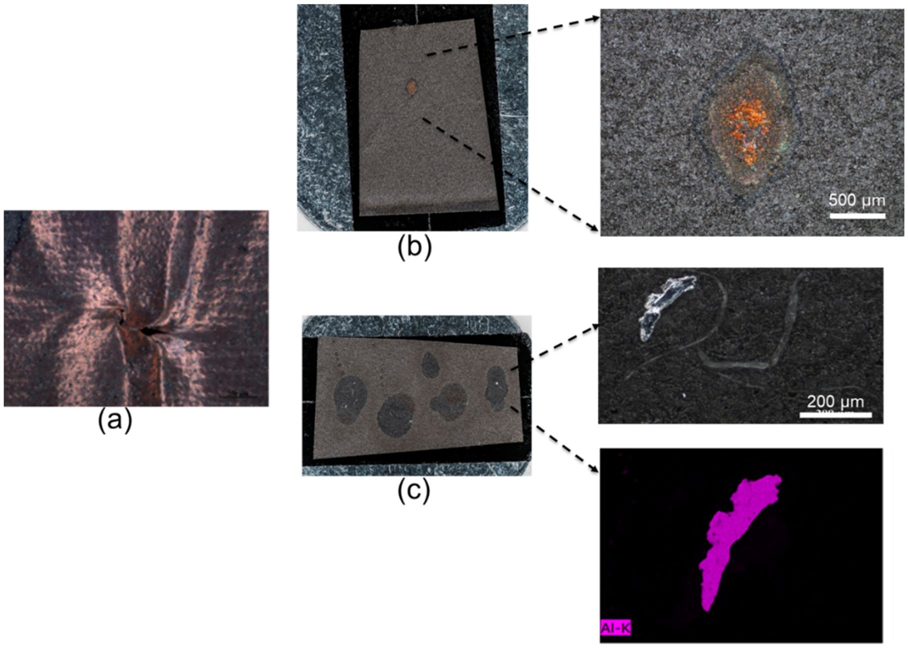


Figure 2. Manufacturing defects and quality control issues causing (a) a hole in the anode current collector and (b, c) impurities in the electrodes.

18650 format cylindrical cells and provides protection against a hard external short. Other cell formats, such as metal-can-prismatic cells, have included protective controls such as fusible links and bimetallic fuses that melt and disconnect, causing the cell to be permanently incapable of being charged or discharged. In the case of pouch format cells that do not have an internal protective device designed into the cell, external short circuit tests have shown to cause the burning of one of the tabs—thus protecting the cell from a catastrophic failure. The tab that is burned off is the one with the lower melting point and is different for various manufacturers (anode or cathode).[24]

The PTCs in cylindrical lithium-ion cells are doughnut-shaped devices that have a conductive polymer sandwiched between two stainless steel discs. Under high currents and high temperatures, these devices get activated due to the expansion of the polymer, which increases the resistance of the device, leading to a reduction in the current going in to or out of the cell. Protective devices such as PTCs have threshold voltage limitations like any electronic device. In the early days of Li-ion battery production, the applications required very low energy and power, and the devices required less than 30 Wh of energy. However, today, applications such as large ESSs are sized in the range of MWh to GWh. Due to the threshold voltage limitations in PTC devices, in off-nominal conditions, these PTCs do not protect as expected but rather become the cause of the hazard.[25,26] This typically leads to excessive charring of the header area of the cells, venting and leakage of electrolyte, and smoke. PTC threshold voltage limitations vary between cell manufacturers and also vary between different models from the same manufacturer.[25,26] In large ESSs, cells with internal protective devices should be proven by test to protect at the relevant level in the design configuration, and other levels of protection should be relied upon for safety control before a cell-level protective device is called in to provide protection.

Internal short circuits occur when the cathode and the anode physically touch each other inside a cell, leading to a short circuit. Internal short circuit hazards can be created in two different ways. Poor manufacturing and lack of quality control can lead to the formation of internal short circuits.[27,28] Figure 2 has examples of defects created and impurities introduced due to lack of quality control during the manufacturing process. Other ways internal shorts can be created are poor design, lack of or improper safety controls, and misuse in the field. The hazards discussed above, namely, over-charge, over-discharge, and external shorts, if not prevented by design, can create an internal short circuit that can lead to a catastrophic thermal runaway.

High-quality manufacturing and configuration control during the manufacturing process can significantly reduce the defects created, leading to a reduced risk of an internal short. Although there is no experimental proof that internal shorts due to manufacturing defects are a hazard, simulations of internal shorts using various methods have shown that Li-ion cells at 100% state of charge (SOC) experience a violent venting, fire, and thermal runaway.[29] Hence, cells used in the manufacturing of large ESSs should be screened and matched with a stringent protocol to prevent poor-quality cells from being introduced into the battery assembly process. Designing a battery with the required levels of safety control and using it within the manufacturer's specification for current, voltage, and temperature reduces the risk of the formation of internal short circuits due to over-charge, over-discharge, and short circuits.

An important factor to be taken into consideration in large ESSs is the effect of arcing, which is encountered with systems higher than 50 V.[30,31] This voltage can be as low as 30 V in low-pressure environments. Hence, adequate protection against arcing and static electricity should be provided for the entire ESS, especially in the area of the connectors, to confirm that no sharp corners or pointed metal features are present that can cause an arc.

Thermal Hazards. High and low temperatures can lead to different unsafe conditions in Li-ion cells and batteries. High temperatures can lead to decomposition of the electrolyte and the solid-electrolyte interface (SEI) layer, destabilization of the cathode and anode that eventually lead to a violent venting, fire, and thermal runaway. Low temperatures increase the viscosity of the electrolyte in a Li-ion cell, reducing the mobility of the lithium ions in the electrolyte. The reduction in ionic conductivity causes the deposition of the ions as dendritic lithium metal due to the reduced ease of intercalation into the anode (Figure 3). This subsequently leads to increased internal cell temperatures, and in the presence of high temperatures due to increased internal resistance, growth of lithium metal dendrites, and the organic flammable electrolytes, the inevitable thermal runaway and fire occurs. Hazardous conditions due to low-temperature charging or operation can be mitigated in large ESS battery designs by including a sensing logic that determines the temperature of the battery and provides heat to the battery and cells until it reaches a value that would be safe for charge as recommended by the battery manufacturer. When heaters are used, the power to the heaters should be controlled to prevent uncontrolled heating due to heater failures.

Figure 3. Lithium dendrites (white whiskers) created during repeated charge at low temperatures. Brown areas are unlithiated graphite (under the current collector fingers), and the gold color is lithiated graphite.

Gradients in temperature in a battery configuration can also lead to an unsafe battery during its usage life. If battery configurations do not have a uniform thermal environment, then the capacity, internal resistance, and the voltage with respect to state-of-charge or depth-of-discharge of the cells in the battery will vary, and increased deviation will be observed during the life of the battery. Thermal gradients larger than 3 °C within a battery pack configuration can lead to deviations in the internal resistance of the cells with cycle and calendar life aging that can lead to significant variations and deviations in performance between the cells that can eventually lead to an unsafe condition of the battery. Thus, a thermal management system is imperative for large batteries, especially those that need to function continuously for several years and where extreme thermal environments will be encountered. The types of thermal management systems are discussed later.

Mechanical Hazards. Vibration, shock, and impact are examples of causes that are of the mechanical nature. Natural disasters such as seismic activity can lead to similar mechanically induced hazards. All three mechanical events induce faults such as disturbances to the internal construction of the cells, breakage of cell tab or intercell connections, contacts between the cathode and anode due to a distortion or tear of the separator, and the creation of other defects that can lead to an internal short circuit or high temperatures, both of which can lead to a catastrophic thermal runaway. Although this type of environmental hazard may be rare during field use (e.g., natural disasters), it can also be encountered during the device's transportation to its final location, and hence the cells and system should be thoroughly inspected before and after installation of the entire system is completed.

Thermal Management of Battery Systems. Irrespective of the chemistry, large battery installations can generate a significant amount of heat during operation. Therefore, a cooling system, which can be either passive (uses heat-absorbing or dissipating materials and the ambient environment and natural convection) or active (uses built-in devices to force the movement of cooling media), is needed. In contrast to small portable batteries, large stationary batteries do not have a comparable surface area to passively dissipate heat through natural convection and can reach unsafe high temperatures if not cooled properly.[32] Therefore, active cooling is a recommended approach for thermal management in large stationary batteries.

Air cooling in the form of bulk enclosure ventilation is the primary technique of battery thermal management for large stationary batteries due to its simplicity and low cost.[32] Ventilation systems are well-understood, simple to implement and manage, and dependable as a technology.[32,33] To minimize temperature differences among the cells in a battery, direct air cooling is not recommended, as it can cause temperature differences within the batteries or spot cooling.[32] Different geometric configurations and various kinds of vent plates and vortex generators attached to the battery racks have been studied to evenly distribute air flow within the battery enclosure to ensure efficient cooling and a uniform temperature distribution.[32,33] Liquid cooling is rare in stationary battery systems even though it is widely used in electric vehicle batteries. Liquid cooling can provide superior thermal management, but the systems are more expensive, complex, and prone to leakages, which restricts their use in large stationary systems.[32] Passive cooling using phase-change materials is also under research but is not used to date in commercial ESS batteries.

A high-fidelity thermal analysis will provide valuable data for not only determining the thermal gradients and reducing them but also providing the critical locations that need to be monitored for safety considerations.

Aging and Safety. Large ESSs are expected to function for many years. Installation and integration of the ESS should take into account the changes that occur due to aging. Studies have shown that the life of a Li-ion battery can be increased significantly if the voltage range used is decreased by even 200 mV at each end.[34] Cycle life studies have shown that degradation of the electrodes is a common occurrence with aging and that delamination of the active material can occur, along with other physical degradation reactions. Off-nominal tests carried out on cells that had undergone various levels of capacity loss indicated that aging does change the nature of the results of off-nominal abuse testing, and cells and batteries aged to about 20% capacity fade do not exhibit catastrophic failures.[16,35] However, the stages of capacity fade less than 17% may exhibit catastrophic failures. In the studies referenced here, it was observed that capacity losses of greater than 20% showed excessive degradation and loss of electrolyte, while those below 17% did not, which explains the difference in behavior under off-nominal conditions. Aging also changes the characteristic SOC versus voltage trend, and hence one needs to take this into account when building the charging, battery management, and power management systems, especially if the voltage is used as an indicator for the SOC.

The aging of the cells and batteries influences their reuse in a second-life application. Batteries used in automotive applications have started making an appearance in a second use, such as for stationary grid storage. Although the second use in large stationary ESSs may be less stressful on the battery, the cells and batteries to be reused need to be studied stringently before installation in a second use. After gaining a thorough understanding of the condition and history of the battery usage in its first life application, one needs to study cells and modules from the battery to determine its health. The cells and modules should be taken from areas that were exposed to the highest deviation in temperature from nominal thermal environments. Destructive analysis of cells and modules will go a long way in determining the level of degradation observed within the cell as well as of other components such as interconnects and cables that go into making the modules and batteries.

Battery Management Systems. All Li-ion batteries, irrespective of the battery voltage and capacity and the number of cells in the battery pack, are designed with a battery management system (BMS). The complexity of the BMS varies widely, depending on the requirements of the battery design as well as the application in which the battery is used. Li-ion cells require cell/cell bank voltage monitoring and control irrespective of the size and design configuration of the battery pack. The BMS does the function of monitoring and controlling the voltage, current, and temperature of the battery. The BMS also carries out the function of cell balancing that provides protection against any single cell going over or under its voltage limit but also extends the life of the battery when cells are electrochemically stabilized and function in a more uniform manner. BMSs used in large ESS installations must be effective in monitoring the system behavior and preventing any deviations from nominal operations. Integration of the BMS with overall control systems for protection and suppression against hazards in instances of off-nominal conditions and verification of the order of the operation should be a priority. An important aspect of the BMS is the ability for the operator to remotely monitor the data in order to recognize off-nominal behavior immediately and also in order to provide first responders and fire fighters the relevant information needed for safe entry into a faulty or failed stationary BESS.

To summarize, the worst-case results under the credible off-nominal conditions that may be encountered by a large ESS should be well studied and well characterized. It is imperative that battery designers and manufacturers keep in mind that the required levels of fault tolerance should be included in battery designs, with the battery being independently fault tolerant. In addition to this, chargers should have their own safety controls so as to not impose a current that is higher than what the battery can handle and should be in constant communication with the battery to determine the health of the cells and the battery system in order to safely charge the system.

Toxic and Combustible Gases. When a large BESS experiences an off-nominal condition, the location in which it is placed must be fully assessed. Release of flammable gases from batteries carries a risk of explosions in BESSs. Immediate ignition of flammable vent gases after release may cause a minor deflagration, whereas a longer accumulation of a large volume of gases and subsequent ignition may cause a large explosion in BESS.[12] Combustible gases released under off-nominal conditions such as fire, smoke, and thermal runaway, if present above the lower threshold limit value (TLV), can cause an explosion. Unpublished research by the authors of this manuscript has shown that, for the cells studied, combustible gases such as hydrogen, carbon monoxide, methane, ethylene, and propylene can be produced in concentrations above the TLV. The gases also need to be assessed for toxicity, as personnel walking into the location can be affected adversely if the volume of toxic gases released is not well known and they are not prepared with the appropriate personal protective equipment (PPE). The worst-case volume of gases released per unit volume under an off-nominal condition should be well assessed in order to provide mitigation strategies for safe handling of an off-nominal event by first responders and fire fighters.

Modeling and Simulation of Abuse Conditions in Large Stationary Grid ESSs. Advanced modeling and simulation (M&S) has immense potential to complement experiments in the safety analysis of Li-ion batteries as an essential component of grid ESSs. For example, modeling failure events such as explosions due to combustion of high-speed, high-energy flammable gases produced during thermal runaway or deflagration due to an off-nominal condition may provide insights into evaluating the effectiveness and designing appropriate ventilation and fire suppression systems. In addition, such modeling capability can provide guidelines for firefighters to respond to failure events safely and effectively.

Several lumped[36−38] and multidimensional[39−41] models for single Li-ion cells have been developed to capture various underlying physical phenomena occurring during thermal runaway, including heat and mass transfer, gas generation, exothermic chemical reactions, electrolyte evaporation, venting of flammable gases, and combustion. In addition, thermal runaway models have been extended to battery packs and modules to characterize cell-to-cell propagation. Thermal network models consider cells as lumped thermal masses connected to each other with a group of thermal resistances representing different modes of heat transfer.[42−44] Several studies have developed higher dimension frameworks by considering conduction and radiation as the only modes of heat transfer between the cells,[45,46] while some others have developed computational fluid dynamics (CFD) simulations to capture the thermal energy transferred to the neighboring cells from the vented gases during thermal runaway.[47]

Despite extensive research on single cells and small-scale battery packs, not much attention has been paid to utilizing M&S for risk assessment in large stationary grid ESSs. M&S tools can help investigate possible hazardous scenarios arising from thermal runaway and propagation or electrolyte leakage from a single or a group of damaged cells and accumulation of toxic, conductive, or flammable gases in the battery systems and ESS containers. In a recent study, Jin et al.[48] developed a CFD simulation of gas explosion hazards within a container-type ESS comprising Li-ion battery modules. Extending thermal runaway and propagation simulations to large stationary grid ESSs comes with numerous challenges due to the coupled and nonlinear nature of the differential equations involved, the complex geometry of ESSs, and the large number of cells and modules in ESSs.

Fire Suppression Systems for Large Stationary Grid ESSs. Adequate fire protection and suppression systems for grid ESSs are critical to minimizing the hazards associated with Li-ion failure events.[49] The major challenges associated with Li-ion battery fire suppression systems are the probability of re-ignition after cessation of the fire suppressant release and continued thermal runaway propagation in battery packs, modules, and battery systems.[49,50]

Extensive research has been done to study the effectiveness of various types of extinguishing agents for Li-ion battery fires. Several studies reported the effectiveness of water-based suppressants in containing fire and preventing re-ignition. Some concerns regarding water-based suppressants are the ability of water to conduct electricity and react with salt ($LiPF_6$) in Li-ion battery electrolyte and form the highly toxic and corrosive hydrofluoric acid (HF). Gaseous extinguishing agents, such as carbon dioxide, Halon-based, HFC-227ea, and Novec 1230, have also been used for suppression of Li-ion battery fires.[49] However, Halon-based suppressants are harmful to the environment,[49,50] and re-ignition is a concern regarding carbon dioxide and HFC-227ea.[51−53] Dry powders are also among the fire suppressants tested for Li-ion battery fire and have shown different effectiveness for different battery chemistries.[54] Aerosol is another extinguishing agent reported to be effective for Li-ion battery fire suppression in a closed environment.[55]

Most of the existing studies have focused on the performance of fire extinguishing agents and fire suppression systems for a single Li-ion cell and small-scale battery packs. A limited number of studies focused on large battery systems. For example, LFP and LNO/LMO Li-ion batteries ranging from a single module to full ESS racks comprising 16 battery modules have been tested, and the effectiveness of water in containing the fire, especially for LFP, has been reported.[56] Thus, more research is required to fully assess the performance and effectiveness of various fire suppression systems and agents on large ESS Li-ion battery fires.

In this work, we have summarized all the relevant safety aspects affecting grid-scale Li-ion BESSs. As the size and energy storage capacity of the battery systems increase, new safety concerns appear. To reduce the safety risk associated with large battery systems, it is imperative to consider and test the safety at all levels, from the cell level through module and battery level and all the way to the system level, to ensure that all the safety controls of the system work as expected. As grid-scale BESSs are expected to function for many years, it is also necessary to understand how the aging of the batteries and other components affects the safety and how the BMS should adapt to the changing characteristics. An important aspect to reducing the risk associated with the large BESS installations is the ability of the operator to remotely monitor the system data and recognize any off-nominal behavior in advance in order to prevent and mitigate hazards to the system. This type of stringent monitoring will also enable the sharing of the relevant information with the first responders and fire fighters that is needed for safe entry into a faulty BESS. More work is still needed on the development of the best mitigation practices for off-nominal conditions, early detection and prevention of thermal runaway propagation, and fire suppression for large-scale batteries.

Judith A. Jeevarajan orcid.org/0000-0003-4843-7597
Tapesh Joshi
Mohammad Parhizi
Taina Rauhala
Daniel Juarez-Robles

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.2c01400.

Table S1, listing reported failure incidents involving BESS installations worldwide since 2011 (PDF)

AUTHOR INFORMATION

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsenergylett.2c01400

Notes

Views expressed in this Energy Focus are those of the authors and not necessarily the views of the ACS.
The authors declare no competing financial interest.

REFERENCES

(1) DOE Global Energy Storage Database. https://sandia.gov/ess-ssl/gesdb/public/statistics.html (accessed April 4, 2022).

(2) Argyrou, M. C.; Christodoulides, P.; Kalogirou, S. A. Energy storage for electricity generation and related processes: Technologies appraisal and grid scale applications. *Renewable Sustainable Energy Rev.* **2018**, *94*, 804−821.

(3) Fan, X.; Liu, B.; Liu, J.; Ding, J.; Han, X.; Deng, Y.; Lv, X.; Xie, Y.; Chen, B.; Hu, W.; Zhong, C. Battery Technologies for Grid-Level Large-Scale Electrical Energy Storage. *Trans. Tianjin University* **2020**, *26* (2), 92−103.

(4) Maisch, M. Zinc-air battery, CHP and PV to power apartment complex in New York. *pv magazine*, Jan 24, 2022https://www.pv-magazine.com/2022/01/24/zinc-air-battery-chp-and-pv-to-power-apartment-complex-in-new-york/ (accessed April 4, 2022).

(5) Kebede, A. A.; Kalogiannis, T.; Van Mierlo, J.; Berecibar, M. A comprehensive review of stationary energy storage devices for large scale renewable energy sources grid integration. *Renewable Sustainable Energy Rev.* **2022**, *159*, 112213.

(6) Hesse, H.; Schimpe, M.; Kucevic, D.; Jossen, A. Lithium-Ion Battery Storage for the Grid—A Review of Stationary Battery Storage System Design Tailored for Applications in Modern Power Grids. *Energies* **2017**, *10* (12), 2107.

(7) Preger, Y.; Torres-Castro, L.; Rauhala, T.; Jeevarajan, J. Perspective—On the Safety of Aged Lithium-Ion Batteries. *J. Electrochem. Soc.* **2022**, *169* (3), 030507.

(8) EPRI BESS Failure Event Database. http://storagewiki.epri.com/index.php?title=BESS_Failure_Event_Database&oldid=1944 (accessed April 7, 2022).

(9) Ji-hye, S. Panel blames electric shock, poor management system for ESS fires, not companies. *The Korea Herald*, June 11, 2019.

(10) Yun-Hwan, C. ESS units caught on fire due to bad management. *Korea JoongAng Daily*, June 11, 2019.

(11) Hyun-woo, N. Firms angry as gov't blames battery cell for ESS fires. *The Korea Times*, February 6, 2020.

(12) Zalosh, R.; Gandhi, P.; Barowy, A. Lithium-ion energy storage battery explosion incidents. *J. Loss Prevention Process Industries* **2021**, *72*, 104560.

(13) Juarez-Robles, D.; Vyas, A. A.; Fear, C.; Jeevarajan, J. A.; Mukherjee, P. P. Overcharge and Aging Analytics of Li-Ion Cells. *J. Electrochem. Soc.* **2020**, *167* (9), 090547.

(14) Kim, C.-S.; Jeong, K. M.; Kim, K.; Yi, C.-W. Effects of Capacity Ratios between Anode and Cathode on Electrochemical Properties for Lithium Polymer Batteries. *Electrochim. Acta* **2015**, *155*, 431−436.

(15) Jeevarajan, J. Safety of Commercial Lithium-Ion Cells and Batteries. In *Lithium-Ion Batteries*, Pistoia, G., Ed.; Elsevier: Amsterdam, 2014; pp 387−407.

(16) Juarez-Robles, D.; Azam, S.; Jeevarajan, J. A.; Mukherjee, P. P. Degradation-Safety Analytics in Lithium-Ion Cells and Modules: Part III. Aging and Safety of Pouch Format Cells. *J. Electrochem. Soc.* **2021**, *168* (11), 110501.

(17) Jeevarajan, J. A.; Cook, J. S.; Davies, F. J.; Salinas, M. J.; Collins, J.; Bragg, B. J. Comparison of Performance and Safety of Two Models of Panasonic Li-ion Batteries, 203rd Electrochemical Society Meeting, Paris, France, Apr 27−May 2, 2003.

(18) Jeevarajan, J. A.; Davies, F.; Lazaroff, S.; Bragg, B. J. Safety Evaluation of Two Commerical Lithium-ion Batteries, Proceedings of the 39th Power Sources Conference, Cherry Hill, NJ, Jun 12−15, 2000.

(19) Fear, C.; Juarez-Robles, D.; Jeevarajan, J. A.; Mukherjee, P. P. Elucidating Copper Dissolution Phenomenon in Li-Ion Cells under Overdischarge Extremes. *J. Electrochem. Soc.* **2018**, *165* (9), A1639−A1647.

(20) Guo, R.; Lu, L.; Ouyang, M.; Feng, X. Mechanism of the entire overdischarge process and overdischarge-induced internal short circuit in lithium-ion batteries. *Sci. Rep.* **2016**, *6* (1), 30248.

(21) Nemanick, E. J.; Wang, D.; Matsumoto, J.; Ives, N. Effects of Cell Reversal on Li-Ion Batteries, 230th Electrochemical Society Meeting, Honolulu, HI, Oct 2−7, 2016.

(22) Zheng, Y.; Qian, K.; Luo, D.; Li, Y.; Lu, Q.; Li, B.; He, Y.; Wang, X.; Li, J.; Kang, F. Influence of over-discharge on the lifetime and performance of LiFePO4/graphite batteries. *RSC Adv.* **2016**, *6* (36), 30474.

(23) Jeevarajan, J. A.; Strangways, B.; Nelson, T. Hazards Due to Overdischarge in Lithium-ion Cylindrical Cells in Multi-cell Configurations, 2010 NASA Battery Workshop, Huntsville, AL, Nov 16−18, 2010.

(24) Joshi, T.; Azam, S.; Lopez, C.; Kinyon, S.; Jeevarajan, J. Safety of Lithium-Ion Cells and Batteries at Different States-of-Charge. *J. Electrochem. Soc.* **2020**, *167* (14), 140547.

(25) Jeevarajan, J. A. Hazards Associated with High Voltage High Capacity Lithium-ion Batteries. *ECS Trans.* **2011**, *33* (22), 1−6.

(26) Manzo, M. A.; Brewer, J. C.; Bugga, R. V.; Darcy, E. C.; Jeevarajan, J. A.; McKissock, B. I.; Schmitz, P. C. *NASA Aerospace Flight Battery Program Part 1 - Vol. II*, Report No. NESC-RP-08-75; NASA Engineering and Safety Center, 2008.

(27) Mohanty, D.; Hockaday, E.; Li, J.; Hensley, D. K.; Daniel, C.; Wood, D. L. Effect of electrode manufacturing defects on electrochemical performance of lithium-ion batteries: Cognizance of the battery failure sources. *J. Power Sources* **2016**, *312*, 70−79.

(28) Cannarella, J.; Arnold, C. B. The Effects of Defects on Localized Plating in Lithium-Ion Batteries. *J. Electrochem. Soc.* **2015**, *162* (7), A1365−A1373.

(29) Hao, W.; Xie, J.; Wang, F. The indentation analysis triggering internal short circuit of lithium-ion pouch battery based on shape function theory. *Int. J. Energy Res.* **2018**, *42* (11), 3696−3703.

(30) Jeevarajan, J.; Manzo, M. *Limitations of Internal Protective Devices in High-Voltage/High Capacity Batteries Using Lithium-Ion Cylindrical Commercial Cells*, NASA Engineering and Safety Center Technical Bulletin, Lesson No. 2046, May 10, 2009.

(31) Augeard, A.; Singo, T.; Desprez, P.; Perisse, F.; Menecier, S.; Abbaoui, M. Arc analysis to the CID of Li-ion battery cells in high-current applications, IEEE 60th Holm Conference on Electrical Contacts, Oct 12−15, 2014.

(32) Hailu, G.; Henke, M.; Petersen, T. Stationary Battery Thermal Management: Analysis of Active Cooling Designs. *Batteries* **2022**, *8* (3), 23.

(33) Liu, H.; Wei, Z.; He, W.; Zhao, J. Thermal issues about Li-ion batteries and recent progress in battery thermal management systems: A review. *Energy Conversion Management* **2017**, *150*, 304−330.

(34) Juarez-Robles, D.; Jeevarajan, J. A.; Mukherjee, P. P. Degradation-Safety Analytics in Lithium-Ion Cells: Part I. Aging under Charge/Discharge Cycling. *J. Electrochem. Soc.* **2020**, *167* (16), 160510.

(35) Juarez-Robles, D.; Azam, S.; Jeevarajan, J. A.; Mukherjee, P. P. Degradation-Safety Analytics in Lithium-Ion Cells and Modules Part II. Overcharge and External Short Circuit Scenarios. *J. Electrochem. Soc.* **2021**, *168* (5), 050535.

(36) Parhizi, M.; Crompton, K. R.; Ostanek, J. Probing the Role of Venting and Evaporative Cooling in Thermal Runaway for Small Format Li-Ion Cells, ASME 2021 International Mechanical Engineering Congress and Exposition (IMECE2021), Nov 1−5, 2021.

(37) Ostanek, J. K.; Li, W.; Mukherjee, P. P.; Crompton, K. R.; Hacker, C. Simulating onset and evolution of thermal runaway in Li-ion cells using a coupled thermal and venting model. *Appl. Energy* **2020**, *268*, 114972.

(38) Coman, P. T.; Rayman, S.; White, R. E. A lumped model of venting during thermal runaway in a cylindrical Lithium Cobalt Oxide lithium-ion cell. *J. Power Sources* **2016**, *307*, 56−62.

(39) Kong, D.; Wang, G.; Ping, P.; Wen, J. A coupled conjugate heat transfer and CFD model for the thermal runaway evolution and jet fire of 18650 lithium-ion battery under thermal abuse. *eTransportation* **2022**, *12*, 100157.

(40) Kim, J.; Mallarapu, A.; Finegan, D. P.; Santhanagopalan, S. Modeling cell venting and gas-phase reactions in 18650 lithium ion batteries during thermal runaway. *J. Power Sources* **2021**, *489*, 229496.

(41) Vendra, C. M. R.; Shelke, A. V.; Buston, J. E. H.; Gill, J.; Howard, D.; Read, E.; Abaza, A.; Cooper, B.; Wen, J. X. Numerical and experimental characterisation of high energy density 21700 lithium-ion battery fires. *Process Safety Environ. Protection* **2022**, *160*, 153−165.

(42) Feng, X.; Lu, L.; Ouyang, M.; Li, J.; He, X. A 3D thermal runaway propagation model for a large format lithium ion battery module. *Energy* **2016**, *115*, 194−208.

(43) Feng, X.; He, X.; Ouyang, M.; Lu, L.; Wu, P.; Kulp, C.; Prasser, S. Thermal runaway propagation model for designing a safer battery pack with 25Ah $LiNi_xCo_yMn_zO_2$ large format lithium ion battery. *Appl. Energy* **2015**, *154*, 74−91.

(44) Jiang, Z. Y.; Qu, Z.; Zhang, J.; Rao, Z. Rapid prediction method for thermal runaway propagation in battery pack based on lumped thermal resistance network and electric circuit analogy. *Appl. Energy* **2020**, *268*, 115007.

(45) Coman, P. T.; Darcy, E. C.; Veje, C. T.; White, R. E. Numerical analysis of heat propagation in a battery pack using a novel technology for triggering thermal runaway. *Appl. Energy* **2017**, *203*, 189−200.

(46) Jia, Y.; Uddin, M.; Li, Y.; Xu, J. Thermal runaway propagation behavior within 18,650 lithium-ion battery packs: A modeling study. *J. Energy Storage* **2020**, *31*, 101668.

(47) Mishra, D.; Shah, K.; Jain, A. Investigation of the Impact of Flow of Vented Gas on Propagation of Thermal Runaway in a Li-Ion Battery Pack. *J. Electrochem. Soc.* **2021**, *168* (6), 060555.

(48) Jin, Y.; Zhao, Z.; Miao, S.; Wang, Q.; Sun, L.; Lu, H. Explosion hazards study of grid-scale lithium-ion battery energy storage station. *J. Energy Storage* **2021**, *42*, 102987.

(49) Yuan, S.; Chang, C.; Yan, S.; Zhou, P.; Qian, X.; Yuan, M.; Liu, K. A review of fire-extinguishing agent on suppressing lithium-ion batteries fire. *J. Energy Chem.* **2021**, *62*, 262−280.

(50) Ghiji, M.; Novozhilov, V.; Moinuddin, K.; Joseph, P.; Burch, I.; Suendermann, B.; Gamble, G. A Review of Lithium-Ion Battery Fire Suppression. *Energies* **2020**, *13* (19), 5117.

(51) Wang, Q.; Mao, B.; Stoliarov, S. I.; Sun, J. A review of lithium ion battery failure mechanisms and fire prevention strategies. *Prog. Energy Combust. Sci.* **2019**, *73*, 95−131.

(52) Liu, Y.; Duan, Q.; Xu, J.; Chen, H.; Lu, W.; Wang, Q. Experimental study on the efficiency of dodecafluoro-2-methylpentan-

3-one on suppressing lithium-ion battery fires. *RSC Adv.* **2018**, *8* (73), 42223−42232.

(53) Wang, Q.; Shao, G.; Duan, Q.; Chen, M.; Li, Y.; Wu, K.; Liu, B.; Peng, P.; Sun, J. The Efficiency of Heptafluoropropane Fire Extinguishing Agent on Suppressing the Lithium Titanate Battery Fire. *Fire Technol.* **2016**, *52* (2), 387−396.

(54) Meng, X.; Yang, K.; Zhang, M.; Gao, F.; Liu, Y.; Duan, Q.; Wang, Q. Experimental study on combustion behavior and fire extinguishing of lithium iron phosphate battery. *J. Energy Storage* **2020**, *30*, 101532.

(55) Ouyang, D.; Chen, M.; Huang, Q.; Weng, J.; Wang, Z.; Wang, J. A Review on the Thermal Hazards of the Lithium-Ion Battery and the Corresponding Countermeasures. *Appl. Sci.* **2019**, *9* (12), 2483.

(56) Ditch, B.; Zeng, D. *Development of Sprinkler Protection Guidance for Lithium Ion Based Energy Storage Systems*; FM Global: Norwood, MA, 2019.