Fundamental Aspects of Large-Scale Energy Storage System Safety

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Abstract:
As the scale of energy storage systems increases, safety considerations grow commensurately with the amount of stored energy. The authors summarize a recent review of safety and reliability findings for battery storage and identify R&D gaps, particularly as batteries are scaled into system level hardware. While there have been a number of studies addressing failure of rechargeable batteries in portable computing and consumer electronics, with a small number of studies on electric vehicle battery systems, in the case of stationary batteries for grid energy storage, very little information exists on the fundamental aspects of safety. The aim of this review is to focus on the R&D needs that will allow the community to build on prior knowledge to address issues of abuse and safety for larger, grid scale energy storage systems. The primary focus of the review will be on the underlying materials science, electrochemical processes, and thermal kinetics that can lead to major safety events. Importantly, consideration will be given to identifying cell and system level interactions, how such interactions manifest into catastrophic failures, and the need to develop mitigation strategies.

To date, the safety of energy storage systems has been looked at almost exclusively through the narrow lens of cell level failures. While a greater understanding of cell level failures has been critical to the success of rechargeable batteries in consumer electronics, the complexity associated with the scale of energy in grid energy storage applications necessitates consideration of a wider range of system level issues related to power electronics, to power conditioning systems and to fire suppression of large energy storage systems and the surrounding physical infrastructure. Furthermore, the kinetic behavior of cell-level failure must take into account the probability of propagation and thermal runaway that is not indicated in smaller batteries of the same chemistry. In this paper, we will first provide a summary on the status of current research and outline the immediate and longer term R&D needs to advance the fundamental safety and reliability needs of the grid energy storage industry.

Keywords: Energy storage; thermal runaway; battery safety.

Introduction

Energy storage inherently has hazards associated with inadvertent release of stored energy. This is true whether the energy is stored as traditional hydrocarbon fuels, subject to fires, as pumped hydroelectric storage, subject to structural failures [1], or electrochemical energy storage subject to thermal runaway. In the case of hydrocarbon fuels, we are familiar with the hazards of fuel fires and developed safety systems to address critical issues. In the case of pumped hydro, we reduced the possibility of dam failures through engineering. In the latter case, thermal runaway of electrochemical energy storage devices has become a more significant issue with increasing system size and higher energy density. Of particular significance in terms of energy density is the prevalence of lithium-ion cells [2] with practical energy densities on the order of 0.5 MJ kg^{-1}. Examples of thermal runaway include lithium-ion cells reviewed in [3] several recent incidents with grid-scale storage facilities [4-6] and transportation systems [7]. One noteworthy aspect of these incidents is the uncertainty of best practices for fire fighting [4].

Factors that can lead to thermal runaway are reviewed in the next section. Recent research on failure in lithium-ion cells is briefly reviewed in the subsequent section. The extension of these results to larger systems is still incomplete, but recent research suggests important considerations as discussed in the section on Understanding failure in larger scale systems.

Factors leading to thermal runaway

The energy stored in electrochemical cells presents a potential source for energy release. Furthermore, electrochemical cells have additional complications relative to other chemical-energy storage systems. More specifically, in most batteries the oxidizing and reducing materials are held in close proximity such that failure of the separator can lead to the release of stored energy. While robust battery management systems can inhibit or reduce the propagation of cell level failures to the larger system, thermal dissipation of heat or the inclusion of reaction-inhibiting additives [8] appear to be the most promising approaches to mitigating thermal runaway when it does occur. Naturally, prevention of runaway is most preferable, and a range of studies have worked to understand possible causes. A range of mechanisms can lead to separator failure, including internal short circuits, mechanical damage and heating that might melt separator materials. Most of these failure mechanisms are reasonably well understood, and cell-level designs such as shutdown separators can reduce but not eliminate their possibility [9].

As will be discussed in the next section, elevated temperatures can lead to exothermic decomposition. Sources of elevated temperatures can include inappropriate installations with inadequate cooling or external thermal forcing from, for example, an external fire source.

While failure probabilities of individual cells are small, the large number of cells assembled into large-scale storage systems increases the probability of local failure, so an important question is the probability of propagation from a failing cell to adjacent cells [10]. In large-scale energy storage systems, the number of control and safety systems is significant, and the probability that point failures can lead to larger system failures can be addressed through probabilistic risk analysis or system-theoretic process analysis [11].

Cell-level lithium-ion studies.

The original prevalent chemistry for lithium-ion cells was based on a carbon anode and a lithium cobalt oxide ($LiCoO_2$) cathode. While this particular chemistry operated without incident under normal conditions, there is potential to go into highly energetic thermal runaway in abnormal scenarios. Significant research has occurred to understand these processes and the industry has moved to more robust cathode materials. Electrode materials based on spinel compounds and iron phosphates are e are significantly less hazardous, and are beginning to supplant $LiCoO_2$ as electrode materials.

Calorimetry measurements have been conducted on a range of cell chemistries, and these identify multiple reaction processes occurring over a range of temperatures [12-15]. Some of these processes are only mildly exothermic while others can lead to thermal runaway where the reaction accelerates through cell disassembly. These measurements provide insight into thermal processes inside cells, showing that measurable heat release can start to occur at temperatures as low as 90 to 120 C. These low temperature reactions have been identified and are primarily caused by the exothermic decomposition of quasi-stable organic lithium salts in the SEI layer [16]. The activation energy for this process has been measured to be in the range of 50 to 100 kJ/mol [17] so that rates increase rapidly with internal or external heating. As the unstable SEI layer decomposes into more stable components, additional lithium and electrolyte are able to react at increased rates as the temperature rises to form additional passivation layers on the anode particle surfaces [18, 19].

In addition to the reactions of the SEI layer, the electrolyte salt, $LiPF_6$, can decompose around 160 to 200 C into LiF and PF_5. PF_5 is a strong Lewis acid that can react with the alkyl carbonate electrolytes forming polymeric chains, or react with trace water to form HF and POF_3 that, in turn, can react to further decompose electrolytes [20].

Though these low temperature reactions are only mildly exothermic, they do result in significant gas generation leading to cell overpressure and potential rupturing of the seals. Measurements suggest that slightly more than 1 L/Ah (STP) of gas is generated during these low temperature processes [8]. Cells are designed so that gases are vented before the overpressure is too great. Vented gases will involve a gaseous jet that will also entrain liquid electrolytes; gases include products of partial oxidation of the alkyl carbonate electrolyte including CO_2 ($\approx$60%), CO, C_2H_4, CH_4 (together $\approx$20%) and H_2 ($\approx$10%) among others [21]. Because the gases and the electrolyte solution are flammable there is the potential for a dramatic burst of flame when venting occurs although this is not observed in all cells.

At somewhat higher temperatures, the cathode is observed to react with the electrolyte. For $LiCoO_2$ cathodes, these reactions start between 120 and 150 C [22] so that this overlaps the anode and electrolyte decomposition reactions. Other cathode materials are observed to react at higher temperatures including $LiMn_2O_4$ and $LiFePO_4$ [14, 15]. These reactions between the cathode and the electrolyte are strongly exothermic.

An important point to be made regarding the potential for heat release in thermal runaway for lithium-ion cells is that the electrolytes are flammable in air and can be oxidized by the cathode at sufficiently high temperatures as well. The energy density of typical alkyl-carbonate electrolytes is in the range of 10-20 MJ kg^{-1}, which is large enough that even the small quantities of electrolyte per cell represent the same energy release potential as the cell itself; that is the electrolyte oxidation potentially releases on the order of 0.5 MJ kg^{-1} [23].

Understanding failure in larger scale systems.

As the scale of the cells and packs increases, the surface to volume ratio decreases and this can reduce the opportunity to dissipate heat that is generated through normal operation or through local failure (i.e. localized internal short circuit). That is, a basic thermal balance between volumetric heat release and surface-area limited heat dissipation leads to a reduced ability to dissipate thermal energy that scales with the inverse of the shortest heat-transfer length scale (i.e. the diameter of a cell or thickness of a pouch). As cells are arranged into packs, modules and systems this shortest effective length scale will tend to increase. Recent work has shown that, while the net energy released in some larger format cells is similar when normalized by the stored energy, the normalized heat release rate increased though details of the construction of different size cells may play a role in this [24].

When multiple cells are arranged into packs, an important concern is the likelihood for single cell failure to propagate through the pack. The potential for propagation through a pack was modeled by Spotnitz et al. [25] and these results pointed out that cell-to-cell propagation is sensitive to the effective heat transfer between cells. This result is supported by testing: thermal runaway between cylindrical cells is less likely to propagate than that between pouch cells that are in more intimate thermal contact [10]. Tests have also shown that the electrical connectivity can affect the likelihood of thermal runaway propagation; specifically, when cells are connected in parallel and not electrically isolated during runaway of one cell, a resulting short circuit in the initially failing cell leads to the release of stored energy from the parallel cells [10]. This suggests the importance of electrical disconnects and fuses for system design.

If the hazard is associated with an external heat source like a fire, there is the potential to have heat flux from this source lead to thermal runaway in batteries. In recent testing the time to heat cells to temperatures where thermal runaway starts was shown to be significant relative to fire detection times, and it is possible to consider sprinkler suppression of fires in the time that it takes to heat the cells to thermal-runaway temperatures [26].

As in the case of the organic electrolytes, structural materials including polymer packaging and separators can provide significant sources of energy for heat release if flammable [23]. Structural materials also offer significant paths for heat dissipation or containment if thermally conducting or insulating.

To date, scientific analysis of hazards associated with large-scale storage systems is largely non-existent. Experimental results are absent from the literature in batteries larger than even a handful of cells. In such an environment, the response to incidents is typically to apply safety measures that are chemistry and design agnostic, and not rigorously evaluated through research. The result is safety that doesn't take into account the specific system needs. This can be counterproductive both in terms of the cost of ineffective fixes and in the failure to address actual risks. A similar situation can occur for first responders where nationally reported incidents may encourage ineffective response strategies for other systems. A significant need exists for a science-based approach for energy storage systems to identify:

- System-specific safety technologies and engineering design practices.
- Processes for response to incidences that might occur.
- Reflection of best practices in codes, standards and regulations.

These best practices must address specific differences among the range of technology options currently under consideration. In this paper only lithium-ion cell safety was discussed because the relevant cell or system level information for other relevant technologies (advanced lead-acid, sodium-sulfur and flow battery systems) are much less studied for off-normal event behavior, despite past accidental fires for both lead-acid and sodium-sulfur systems [4-6]. To achieve the needs listed above for stationary system scale technology the gap from cell and small string abuse testing must be supplemented by empirical studies up to larger pack designs, for a range of chemistries and for a range of scenarios. These results must be coupled with modeling efforts. Furthermore, ancillary systems including power electronics must be considered for evaluating risk and consequences in off-normal events. Finally, risk assessment must be incorporated along with mitigating factors such as location, adjacent material, ventilation, suppression and containment integrated into design, as well as first responder guidance. Such assessments must consider conflagration, thermal release, gas and spray release. Together this represents a significant research and development challenge.

Summary

In this paper a brief summary of existing safety issues existing for rechargeable batteries as energy storage systems is outlined. Hazards associated with individual lithium-ion cells and their component materials have been studied most extensively and this has led to material science improvements that are expected to contribute to safer energy storage in the future. However, studies for larger systems are extremely limited as are studies of alternate chemistries relevant for grid energy storage. The costs of larger systems suggest a comprehensive science and engineering approach to understand components and their assembly into systems that might minimize the most costly tests and accidents. This approach should involve coupled experimental and modeling aspects and should address the diversity of storage system chemistries and design approaches that exist and are being considered.

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References

[1] J. L. Ehasz and K. Paul, "Taum Sauk Upper Reservoir Failure: Report On Technical Reasons for the Breach," Bonneville Power Administration, 2006.

[2] B. Scrosati and J. Garche, "Lithium batteries: Status, prospects and future," *Journal of Power Sources,* vol. 195, pp. 2419-2430, May 1 2010.

[3] Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, and C. Chen, "Thermal runaway caused fire and explosion of lithium ion battery," *Journal of Power Sources,* vol. 208, pp. 210-224, Jun 15 2012.

[4] U. Irfan, "Battery Fires Pose New Risks to Firefighters," in *ClimateWire*, http://www.scientificamerican.com/article/battery-

fires-pose-new-risks-to-firefighters/: Scientific American, 2015.

[5] J. Ferguson, "APS fire probed," http://azdailysun.com/news/local/aps-fire-probed/article_1de2e924-ab0a-5e71-9a3a-6942c2d1c9bb.html: Arizona Daily Sun, 2013.

[6] NGKinsulators, "Cause of NAS Battery Fire Incident, Safety Enhancement Measures and Resumption of Operations," http://www.ngk.co.jp/english/news/2012/0607.html, 2012.

[7] J. Lowy. (2013, 8-7-2014). *Overcharging batteries eyed in Boeing 787 mishaps.*

[8] G. Nagasubramanian and C. Orendorff, "Hydrofluoroether electrolytes for lithium-ion batteries: Reduced gas decomposition and nonflammable," *Journal of Power Sources,* vol. 196, pp. 8604-8609, Oct 15 2011.

[9] P. G. Balakrishnan, R. Ramesh, and T. P. Kumar, "Safety mechanisms in lithium-ion batteries," *Journal of Power Sources,* vol. 155, pp. 401-414, Apr 21 2006.

[10] J. Lamb, C. J. Orendorff, L. A. M. Steele, and S. W. Spangler, "Failure propagation in multi-cell lithium ion batteries," *Journal of Power Sources,* vol. 283, pp. 517-523, Jun 2015.

[11] D. Rosewater and A. Williams, "Analyzing system safety in lithium-ion grid energy storage," *Journal of Power Sources,* vol. 300, pp. 460-471, Dec 2015.

[12] D. D. MacNeil, T. D. Hatchard, and J. R. Dahn, "A comparison between the high temperature electrode/electrolyte reactions of LixCoO2 and LixMn2O4," *Journal of the Electrochemical Society,* vol. 148, pp. A663-A667, Jul 2001.

[13] D. D. MacNeil, D. Larcher, and J. R. Dahn, "Comparison of the reactivity of various carbon electrode materials with electrolyte at elevated temperature," *Journal of the Electrochemical Society,* vol. 146, pp. 3596-3602, Oct 1999.

[14] E. P. Roth, C. C. Crafts, D. H. Doughty, and J. McBreen, "Advanced Technology Development Program for Lithium-Ion Battereis: Thermal Abuse Performance of 18650 Li-Ion Cells, SAND2004-0584.," Sandia National Laboratories2004.

[15] D. D. MacNeil, Z. H. Lu, Z. H. Chen, and J. R. Dahn, "A comparison of the electrode/electrolyte reaction at elevated temperatures for various Li-ion battery cathodes," *Journal of Power Sources,* vol. 108, pp. 8-14, Jun 1 2002.

[16] D. Aurbach, B. Markovsky, I. Weissman, E. Levi, and Y. Ein-Eli, "On the correlation between surface chemistry and performance of graphite negative electrodes for Li ion batteries," *Electrochimica Acta,* vol. 45, pp. 67-86, 1999.

[17] Z. H. Chen, Y. Qin, Y. Ren, W. Q. Lu, C. Orendorff, E. P. Roth*, et al.*, "Multi-scale study of thermal stability of lithiated graphite," *Energy & Environmental Science,* vol. 4, pp. 4023-4030, Oct 2011.

[18] M. Broussely, S. Herreyre, P. Biensan, P. Kasztejna, K. Nechev, and R. J. Staniewicz, "Aging mechanism in Li ion cells and calendar life predictions," *Journal of Power Sources,* vol. 97-8, pp. 13-21, Jul 2001.

[19] B. Y. Liaw, E. P. Roth, R. G. Jungst, G. Nagasubramanian, H. L. Case, and D. H. Doughty, "Correlation of Arrhenius behaviors in power and capacity fades with cell impedance and heat generation in cylindrical lithium-ion cells," *Journal of Power Sources,* vol. 119, pp. 874-886, Jun 1 2003.

[20] S. E. Sloop, J. K. Pugh, S. Wang, J. B. Kerr, and K. Kinoshita, "Chemical reactivity of PF5 and LiPF6 in ethylene carbonate/dimethyl carbonate solutions," *Electrochemical and Solid State Letters,* vol. 4, pp. A42-A44, Apr 2001.

[21] E. P. Roth and C. J. Orendorff, "How Electrolytes Influence Battery Safety," *Electrochemical Society Interface,* vol. 21, pp. 37-41, Summer 2012.

[22] D. D. MacNeil and J. R. Dahn, "Test of reaction kinetics using both differential scanning and accelerating rate calorimetries as applied to the reaction of LixCoO2 in non-aqueous electrolyte," *Journal of Physical Chemistry A,* vol. 105, pp. 4430-4439, May 2001.

[23] P. Ribiere, S. Grugeon, M. Morcrette, S. Boyanov, S. Laruelle, and G. Marlair, "Investigation on the fire-induced hazards of Li-ion battery cells by fire calorimetry," *Energy & Environmental Science,* vol. 5, pp. 5271-5280, Jan 2012.

[24] C. J. Orendorff, J. Lamb, L. A. M. Steele, S. W. Spangler, and J. Langendorf, "Quantification of Lithium-ion Cell Thermal Runaway Energetics, SAND2016-0486," Sandia National Laboratories2016.

[25] R. M. Spotnitz, J. Weaver, G. Yeduvaka, D. H. Doughty, and E. P. Roth, "Simulation of abuse tolerance of lithium-ion battery packs," *Journal of Power Sources,* vol. 163, pp. 1080-1086, Jan 2007.

[26] B. Ditch, G. Yee, and M. Chaos, "Estimating the time-of-involvement of bulk packed lithium-ion batteries in a wharehouse storage fire," in *Fire Safety Science, Proceedings of the Eleventh International Symposium*, New Zealand, 2014.