Application of Fluid Protection for Increased Safety and Efficiency of Lithium-Ion Battery and Electronic Devices

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INTRODUCTION

Lithium-ion batteries are in widespread use worldwide in a vast array of electronic and electric devices ranging from hybrid and electric vehicles to power tools, portable computers and mobile devices. The worldwide market of $28 billion in 2013 is growing rapidly and could reach $41 billion by 2018[1]. While generally safe and reliable energy storage devices, lithium-ion batteries are subject to catastrophic failure known as thermal runaway[2] under certain conditions. Thermal runaway is a series of internal exothermic reactions that are triggered by heat. The creation of excessive heat can be from electrical over-charge, thermal over-heat, or from an internal electrical short. Internal shorts are typically caused by manufacturing defects or impurities, dendritic lithium formation[3] and mechanical damage. While there is typically protective circuitry in the charging devices and in the battery packs that will disable the battery in the event of overcharging or overheating, it cannot protect the battery from internal shorts caused by internal defects or mechanical damage.

The focus of the work described herein is on mitigating the danger caused by thermal runaway resulting from mechanical damage and external heat. However, it is important to note that the energy released in a thermal runaway event is determined primarily from the electro-chemical composition and charge level of the battery[2] and for a given lithium battery, is essentially the same regardless of the trigger. While this study focused on mechanically induced shorts to initiate the event, the immersion technology would be equally effective with internal shorts resulting from other thermal runaway triggers such as internal defects or dendritic lithium formation.

Testing was performed on two battery pack configurations containing either three or six 18650 type lithium-ion cells. A nail puncture of a single cell caused an instantaneous thermal runaway event in the initiating cell. In an unprotected standard air atmosphere this high energy event has been found to increase the temperature of adjacent cells and to cause them to subsequently enter thermal runaway creating a cell-to-cell cascading thermal runaway event significantly more energetic than the initial event. Immersing the battery packs in a dielectric fluid or applying the fluid at a later time and performing the same nail puncture test, it has been observed that the maximum temperature caused by the thermal runaway event of the initiating cell was reduced by half and the more significant cell-to-cell cascading thermal runaway event was completely avoided.

This has significant potential to provide fire and thermal runaway protection for devices that utilize lithium-ion battery packs, bulk transportation and storage of new and recycled lithium-ion batteries. Transportation vehicles that derive primary or auxiliary electrical energy from lithium-ion batteries including airplanes, electrical vehicles, cargo carriers and trains, could benefit from this technology.

EXPERIMENTAL

Battery cell

All testing used 2.0 Ah, type 18650 lithium-ion batteries utilizing $LiCoO_2$ cathode and graphite anode construction. The electrolyte solvent was 1M $LiPF_6$ in ethylene carbonate:ethyl methyl carbonate (3:7 by vol). The AC impedance at 1 KHz for a single 18650 cell is approximately 40 mΩ. The average open cell voltage was 4.1 V at time of test.

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[1] Murray, C., 2014. Design News – News – Growth Could Be on the Way for Lithium-Ion Battery Market. [online] Available at: http://www.designnew.com/document.asp?

[2] A. Golubkov, D. Fuchsa, J. Wagnerb, H. Wiltschec, C. Stangld, G. Faulerd, G. Voitice, A. Thalera and V. Hackere, 2014, *Thermal-Runaway Experiments on Consumer Li-Ion Batteries with Metal-Oxide and Olivine-Type Cathodes*, RSC Adv., 4, 3633-3642

[3] J. Wen, Y. Yu and C. Chen, 2012, *A Review on Lithium-Ion Batteries Safety Issues: Existing Problems and Possible Solutions,* Mater. Express, 2, 197-212

The battery pack configurations are as follows:

Six 18650 lithium-ion cells were configured with two groups in series with each group consisting of three cells in parallel. This configuration was designated 3P2S. The configuration with three 18650 cells in parallel was designated 3P. See figure 1 for configuration schematics.

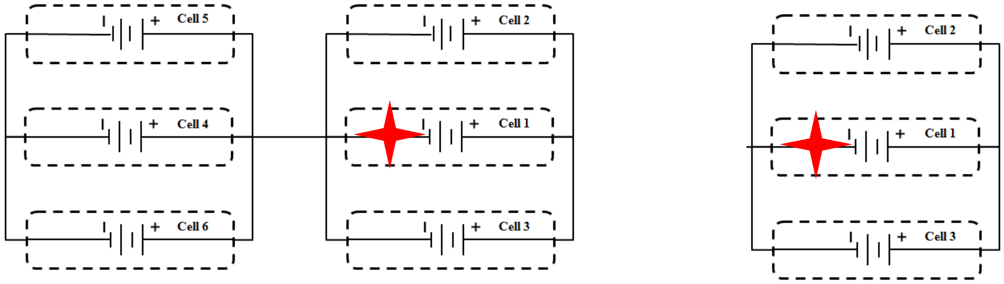

Figure 1: 3P2S Battery Pack Configuration (left) and 3P configuration (right)

Fluid Description The tests and data described in this report were conducted using a fluorinated ketone dodecafluoro-2-methylpentan-3-one also referred by the AHRI nomenclature FK-5-1-12. Other fluids have been tested with similar results and show potential to be utilized in this application. Other dielectric fluids that are liquid at or near the operating temperature range of the battery could also be effective. These include, though are not limited to, fluorinated organic compounds such as, hydrochlorofluorocarbons, hydrofluorocarbons, perfluorocarbons, perfluorinated amines, partially fluorinated ethers, hydrofluoroethers, and hydrofluorolefins.

Test Configuration

The test fixture consisted of a stepper motor that lowered a metal rod with a conical tip (nail) until it pierced a single cell, causing an internal short, instant thermal runaway within the cell and a subsequent explosion that vented high temperature materials and flammable organic solvents. The battery packs were secured in a stainless steel container that allowed for a variable amount of fluid to be in direct contact with the exterior surface of the lithium-ion cells in the battery packs.

Multiple rounds of testing were performed on individual cells as well as battery packs consisting of multiple cells. This report will focus on the results of three representative battery pack tests for clarity.

> Test 1: A 3P2S battery pack was placed in the test fixture with no fluid present (3P2S dry). The nail puncture was on cell 1 as shown in figure 1 with location depicted with a red star.
>
> Test 2: A 3P2S battery pack was fully immersed in the fluid (3P2S wet). The nail puncture was on cell 1 as shown in figure 1 with location depicted with a red star. The ratio between the volume of the fluid and the volume displaced by the cells was approximately 8:1.
>
> Test Series 3: A 3P battery pack was not immersed in the fluid at the time of the initial mechanically induced failure. The nail puncture was on the center cell 1 as shown in figure 1 with location depicted with a red star. Fluid was dispensed into the container at various times after the initial nail puncture.

Data Acquisition

Video and thermal imaging of the lithium-ion cells was recorded during the test. Type K thermocouples were secured with thermal tape to each cell surface. Additional thermocouples were placed in the surrounding air or fluid spaces to capture ambient temperatures. Temperature data were then collected before, during and after the thermal events.

RESULTS

The result of test 1 with the dry (no fluid present) 3P2S pack is shown in Chart 1. The initial mechanically induced, internal thermal runaway event generates a significant amount of heat at cell 1 with a measured surface temperature of 490°C. The cell-to-cell cascading thermal runaway was observed to propagate to adjacent cell number 2 approximately 150 seconds later with an increased maximum surface temperature of 647°C. Approximately 200 seconds after the event at cell 2 the final thermal runaway event occurred in cell number 3 reaching a maximum surface temperature of 679°C. The failures at cells 2 and 3 were caused entirely by external heat and were observed to increase in severity relative to the initial mechanical failure caused by the nail at cell 1. Interestingly, the cell-to-cell thermal runaway never propagated from the group containing cells 1, 2 and 3 to the group with cells 4, 5 or 6, see figure 1. This could be due to significantly less surface area shared between the two groups compared with cells within a group.

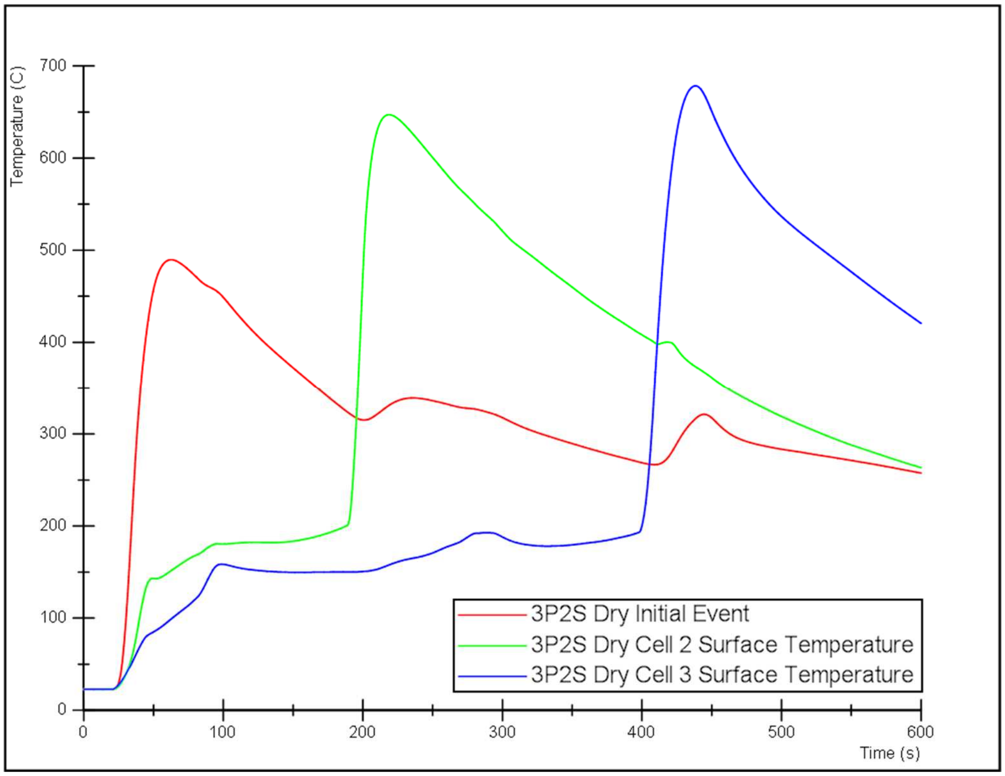

Chart 1: Test 1 Results

Test 2 was configured similarly to Test 1 but with the battery pack immersed in the fluid. The results of Test 2 are shown below in Chart 2. The initial mechanically induced, within-cell thermal runaway event releases a similar amount of heat energy at cell 1; however, much of the heat was absorbed and dissipated by the surrounding fluid, increasing the fluid temperature by about 25°C. The measured surface temperature of cell 1 only reached 223°C. Subsequent cell-to-cell cascading thermal runaway was eliminated and the resulting surface temperatures of the other cells in the pack were uniform and never exceeded 49°C.

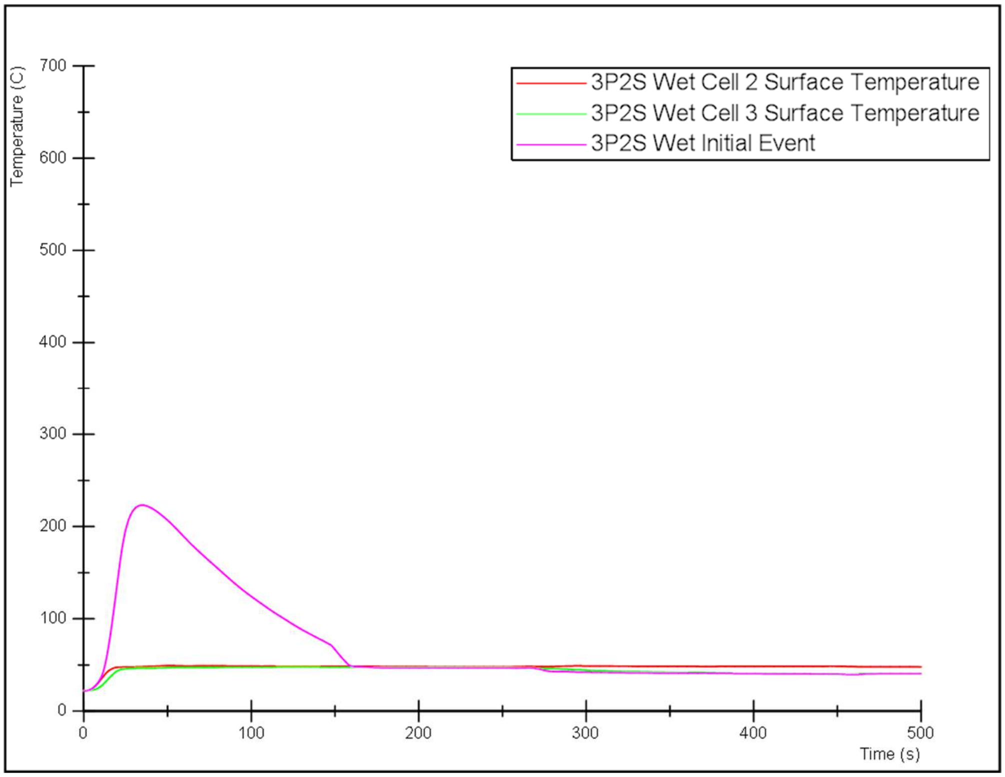

Chart 2: Test 2 Results

Test 3 was configured similarly to Test 2 but with a 3P battery pack that was initially not immersed in the fluid. The initial mechanically induced internal thermal runaway event releases an amount of heat energy at the initial cell similar to Test 1. However, at approximately 72 seconds the fluid is introduced to the test chamber and immediately absorbs much of the heat generated from the initial cell. The measured surface temperature of the adjacent cells reached approximately 100°C before being cooled upon arrival of the fluid to approximately 49°C. Subsequent cell-to-cell cascading thermal runaway was eliminated and the resulting surface temperatures of the all of the cells in the pack became uniform and never exceeded 49°C once fluid was introduced.

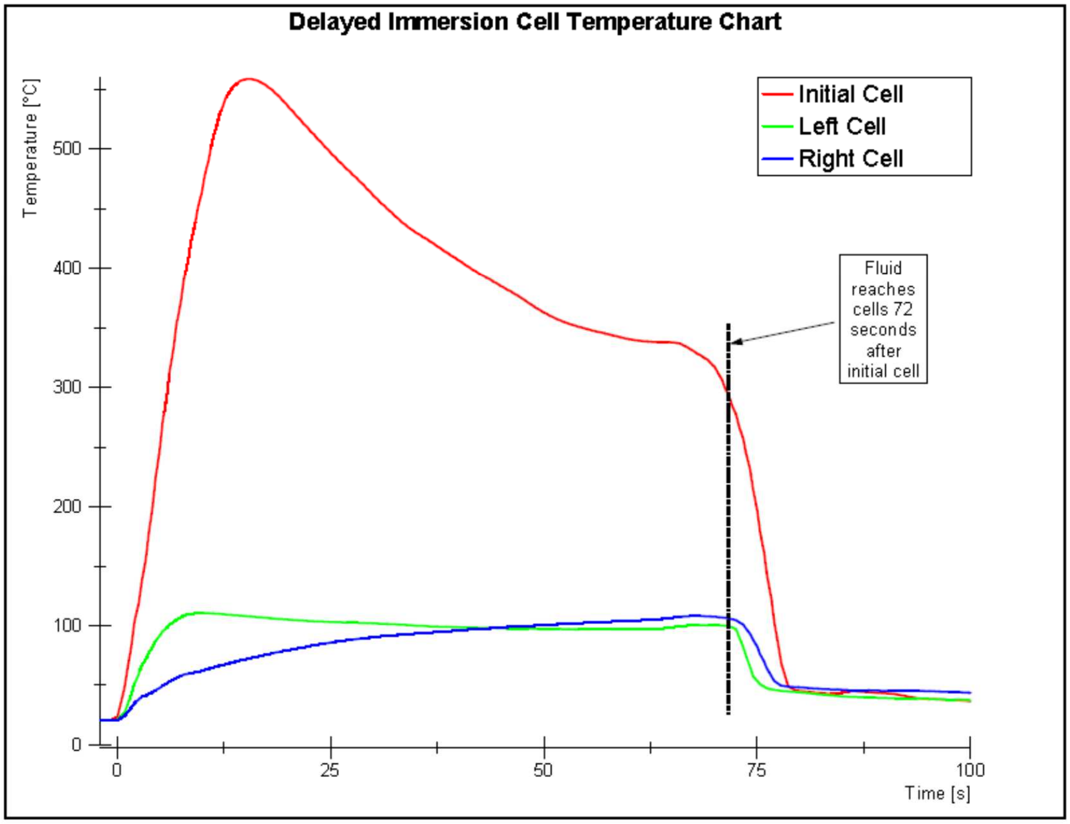

Chart 3: Test Series 3 Results

DISCUSSION:

Thermal runaway is a rapid, almost vertical, temperature increase that is followed by a slow cooling period after the event. The cell surface temperature where thermal runaway started can be seen in chart 4. For clarity of cell to cell comparison, the cell temperature curves had a time offset applied such that the thermal runaway in each cell event began at the same time. In test 1 a surface temperature of 679°C was reached followed by a rapid increase at a rate of 10°C/s.

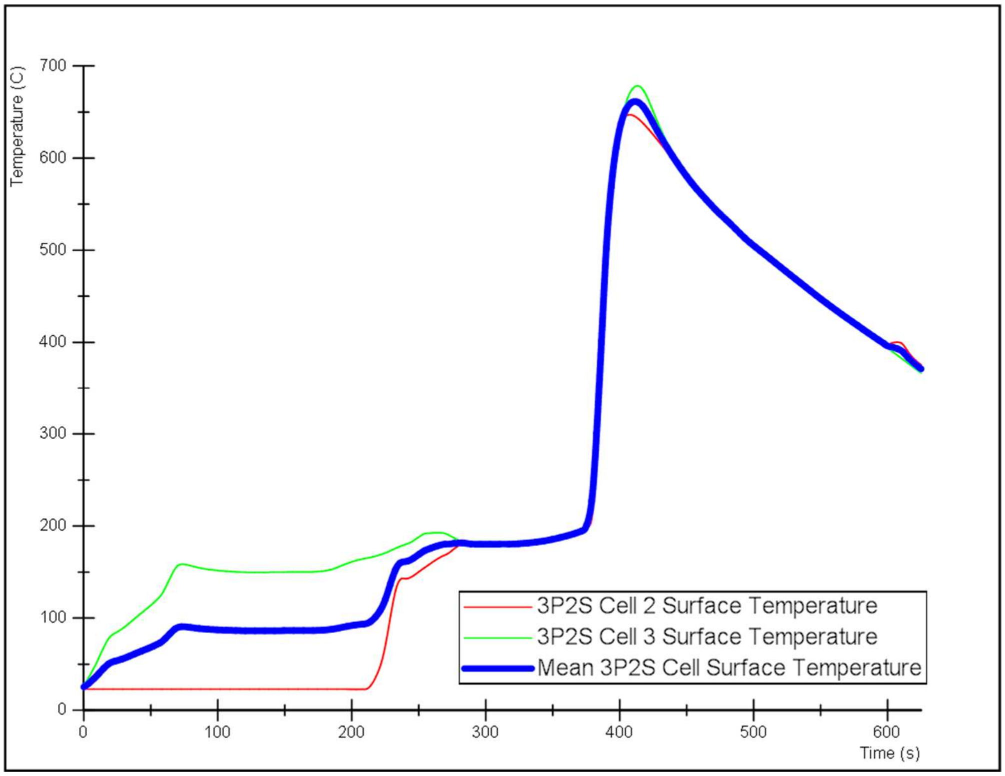

Chart 4: Test 1 Cells 2 and 3 Surface Temperatures

Comparing results from the various immersion experiments that prevented cell-to-cell cascading thermal runaway with the results from the experiments where thermal runaway occurred, it became clear that there is a critical amount of fluid that is required to prevent cell-to-cell thermal runaway. A general volume ratio can be defined by using the following equation (1).

(1) $VR = V_{fluid} / V_{cell}$

Where:
VR = Volume Ratio; V_{fluid} = Volume of the fluid (mL); V_{cell} = Volume of the lithium-ion cells (mL)

For experiments that had a VR less than 2 the cell-to-cell cascading thermal runaway was not prevented. It was found that in the experiments with VR greater than or equal to 8 the system was effective in preventing cascading thermal runaway.

The average surface temperature of all cells that entered heat-induced thermal runaway is shown for each experiment. Key differences between the three tests are highlighted below.

- Test 1 is unprotected 3P2S configuration, reaching a maximum average temperature of 661°C.
- Test 2 is fully protected 3P2S configuration, immersed in fluid with a volume ratio of 8, reaching a maximum average temperature of 48°C.

- Test 3 is a 3P configuration initially unprotected. Fluid is then applied to the cells at various times after the initial cell failure. After an initial cell failure, a variable period of time (between 5 second to 240 seconds) was observed for thermal runaway to occur in one of the adjacent cells. In all tests, cell to cell thermal runaway was prevented from spreading to adjacent intact cells once the fluid was present.

APPLICATIONS

Lithium-Ion Battery Protection

The experimental test data generated for this report came from tests run in an open bath test fixture. Other methods of providing fluid contact to batteries to prevent thermal runaway could include, though are not limited to:

- Fluid stored in a heat sensitive bag that would release the fluid at a specific temperature
- Fluid stored in a separate reservoir and applied to cells via mechanical pumping or superpressurization of the reservoir before or after they enter thermal runaway.
- Fluid stored in a sealed jacket or housing encapsulating the lithium-ion cell or battery pack
- Fluid stored within a sealed compartment within the lithium-ion cell or battery pack

Lithium-Ion Battery Protection and Thermal Management Systems

A thermal management system for lithium-ion battery packs is often required to maximize the life cycle of lithium-ion batteries. This type of system maintains uniform temperatures of each cell within a battery pack. High temperatures can increase the fade and impedance of lithium-ion batteries while decreasing their lifespan. Ideally, each individual cell within a battery pack will be at the same ambient temperature.

The fluid immersion of batteries can mitigate low probability, but catastrophic, thermal runaway events while also providing necessary ongoing thermal management for the efficient normal operation of the lithium-ion battery packs. This new type of application provides thermal management when the fluid is used with a heat exchange system to maintain a desirable operational temperature range. However, in the event of mechanical damage or an internal short of any of the lithium-ion cells, the fluid would also prevent a significant thermal runaway event that could involve most or all of the batteries.

Fire Protection and Thermal Management Systems

Additional applications, beyond lithium-ion batteries, have benefited from fluid immersion technology for thermal management. Hydrofluoroethers and fluoroketones are two example chemistries that have been used for many years in heat transfer applications that require properties such as high dielectric strength, low electrical conductivity, thermal stability, non-flammability and good thermal properties. These fluids have found use in many thermal management applications that include semiconductor manufacturing, electronics cooling (e.g. power electronics, transformers and computers/servers) as well as lithium-ion batteries.

Thermal management systems based on fluid immersion would also provide excellent fire protection properties when the heat transfer fluid utilized has fire extinguishing properties. Energy Storage Systems (ESS) utilizing lithium ion batteries are quickly becoming a critical resource for electric utility companies. IHS Technology, a market research firm, predicts that by 2017 the annual installation of ESSs will be six gigawatts[4].

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[4] J. Roman, (2015, December). *Power to Spare.* NFPA Journal, 40-48.

CONCLUSIONS

The wide-spread adoption and use of lithium-ion batteries coupled with the potentially catastrophic failure mode of thermal runaway has created a fire safety issue that requires a solution. Lithium-ion batteries present a significant fire hazard that can be caused by external heat, mechanical failure or internal shorts. These explosive thermal events initiate in a single cell but when that cell is in a battery pack, the potential for a cell-to-cell cascading thermal runaway is created. It has been observed in these experiments that failure caused by cell-to-cell cascading thermal runaway is more catastrophic in terms of energy release than a single mechanical failure in lithium-ion batteries. However, in applications such as in transportation and storage of lithium-ion batteries as well as electric vehicles, airplanes, cargo vehicles, trains, etc., mechanical failure cannot always be avoided. Catastrophic damage caused by mechanical failure and internal shorts must be contained or mitigated. Lithium ion battery technology has outpaced regulatory bodies, and there currently is no a standard covering this hazard or its protection. In light of this, the Fire Protection Research Foundation collaborated with the FDNY to hold a safety workshop with experts in November, 2015, to address the hazard. Unfortunately, the desire for a conventional fire suppression method is insufficient for the protection of what is essentially a non-fire heat transfer technology challenge. If heat transfer from the initial cell is mitigated, the fire hazard is eliminated.

Fluid immersion technology of lithium-ion batteries has been proven in concept to mitigate this safety hazard. The experiments described in this report clearly show that when immersed in a sufficient volume of a fluorinated ketone, the maximum temperature of a lithium-ion cell was reduced by half and the more significant cell-to-cell cascading thermal runaway event was completely avoided. Additionally, the method of time delayed application of the fluid was effective in stopping cell-to-cell thermal runaway, though no set time delay was able to be established due to the variability in the time period it took for an adjacent cell to fail after the initial failure. In general, applying the fluid sooner will result in lower overall temperatures and fewer number of failed cells. However, at any point in time between the initial event and the final cell failure, application of the fluid has a very positive effect in dissipating heat energy from the cells at risk preventing any further thermal runaway.