

MAKING LITHIUM-ION SAFE THROUGH THERMAL MANAGEMENT

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Abstract

Lithium-ion batteries have revolutionized the portable electronics industry by offering significantly higher energy density and specific energy than other battery technologies. Lithium-ion is now transitioning from its pigeonhole in portable applications to become a factor in the transportation and stationary storage markets. The only problems? High costs and a tendency to catch on fire. The cost issue is significant, but not a show stopper for many applications that demand low weight, low volume and no maintenance. The tendency for combustion, however, significantly limits the applications where lithium-ion can be implemented as well as how it can be shipped.

Complex cooling systems have been developed for automotive lithium-ion batteries, but as evidenced by the Chevy Volt fire and Fisker Karma recall, they may actually cause more harm than good. To simplify the approach, phase change material (PCM) can be used to encase lithium-ion cells. PCMs have the ability to absorb a high amount of heat in a small volume. If one cell goes into thermal runaway, PCM absorbs and wicks away heat to prevent a domino effect within the pack. In some cases, the heat is removed quickly enough to prevent the first cell from combusting.

The paper will discuss the technical aspects of how PCM is able to prevent the propagation of thermal runaway and present modeling and testing data performed by AllCell and the National Renewable Energy Laboratory.

Introduction

A wide variety of energy storage options are available today for the stationary power market; fuel cells, capacitors, compressed air, pumped hydro, flywheels and rechargeable batteries are all vying for a stake in the emerging role of energy storage. Each has its own merits based on a variety of application specific factors.

Within the battery domain, a number of technologies, old and new, are competing for industry dominance in the short-term and long-term. The immediate battle in many applications seems to be lead acid versus lithium-ion. Lithium-ion batteries are considered an enabling technology for many portable applications, but have yet to see widespread adoption in the stationary market compared to lead acid. Figure 1 shows how lead acid and lithium-ion fit into the scheme of rechargeable batteries.

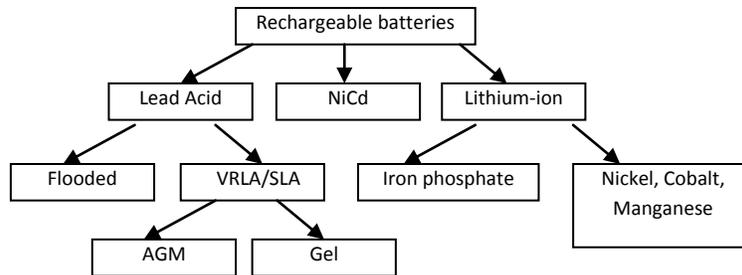


Figure 1. Diagram of Rechargeable battery types

Currently, the stationary market is dominated by lead acid batteries due to their low initial cost, high availability and proven performance history. Lithium-ion is emerging as a contender in stationary applications where volume, weight, temperature sensitivity or low maintenance is more important than initial cost. Table 1 provides a brief comparison of lead acid to lithium-ion on a pack level. It should be noted that both chemistries have a wide range of parameter values, so this table is only a simple representation of a very complex comparison.

Table 1. Battery Technology Comparison

	AGM lead acid	Lithium-ion
Energy Density (Wh/L)	100	250
Specific Energy (Wh/kg)	40	150
Initial Cost (\$/kWh)	120	600
Cycle Life	1,800 @ 30% DoD	2,000 @ 80% DoD
Typical state of charge window	30%	80%
Temperature sensitivity	Degrades significantly above 25°C	Degrades significantly above 50°C
Efficiency	100% @20-hr rate 80% @4-hr rate 60% @1-hr rate	100% @20-hr rate 100% @4-hr rate 98% @1-hr rate
Voltage increments	2 V	3.7 V

The number of obstacles to rapid lithium-ion adoption are numerous as they include technical, logistical and economic factors, so this paper will only touch lightly on those issues while the primary focus will be on the safety concerns surrounding lithium-ion batteries.

Basics of lithium-ion

The concept of a lithium-ion battery was initially conceived in the 1970's and began to see widespread adoption by the 1990's. The basic mechanism is that a charged lithium ion is shuttled back and forth between the cathode and the anode during charge and discharge. Figure 2 shows a diagram of a LiCoO₂ variation of the lithium-ion family.

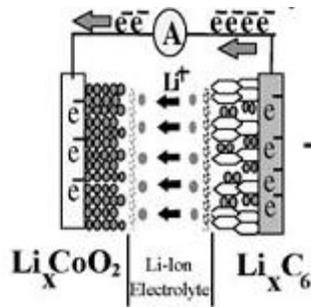


Figure 2. Lithium-ion Reaction¹

Chemistry differences in the cathode, anode, and electrolyte influence cell performance, as does packaging geometry. The cathode chemistry is the factor most commonly altered from cell manufacturer to cell manufacturer with terms like LFP, NCM, NCA, Cobalt, and Manganese reflecting specific cathode types. Over 90% of lithium-ion anodes are comprised of graphite, with silicon and titanium based materials sometimes being used.

Electrolyte exists in liquid form, but for “lithium polymer” cells, the electrolyte is absorbed in a polymer membrane. This allows for cell manufacturers to use a pouch enclosure on the cell rather than the metal casing used when liquid electrolyte is present in cylindrical and prismatic shaped cells. Each of these variations influences the safety of a lithium-ion cell.

In spite of the various chemical variations, lithium-ion batteries can be roughly separated into two groups: lithium iron phosphate (LFP, LiFePO_4) and mixed metal (NCM, NCA, Cobalt, Manganese). Table 1

Table 2 outlines differences between the two chemistry classes on a cell level.

Table 2. Lithium-ion Subcategory Comparison

	LiFePO4	LiNCM
Voltage	3.3 V nominal (2-3.6 V/cell)	3.7 V nominal (2.7-4.2 V/cell)
Energy Density	300 Wh/L	735 Wh/L
Specific Energy	128 Wh/kg	256 Wh/kg
Power	1000 W/kg	512 W/kg
Cycle Life	2,500	1,800
Calendar Life	6 years	8 years
Max recommended temperature	40°C	55°C
Safety	High	Moderate
Suppliers	A123, Valence, IB, BYD, K2, Lishen, many Chinese vendors	Sanyo, Panasonic, Samsung, DowKokam

Safety Concerns

Based on the lithium-ion comparison table, the technology features are very attractive for many stationary applications. However, lithium-ion cells have the potential to go into “thermal runaway” where the cell can combust and emit flames and gases. The consequences of cell combustibility and inadequate containment measures have been exhibited in the form of electric vehicle fires, laptop explosions, plane crashes caused by battery fires, and numerous other incidents. These incidents, rightly, have led to increased regulations on battery cell and pack safety testing, packaging and certification processes.

In some cases the specific cause of the incident is known, while others remain unknown. Figure 3 shows the various trigger mechanisms as well as the process that leads to explosion and fire. Thermal runaway can be triggered by external and internal factors and the severity of the event is dependent upon cell and pack level chemistry and design.

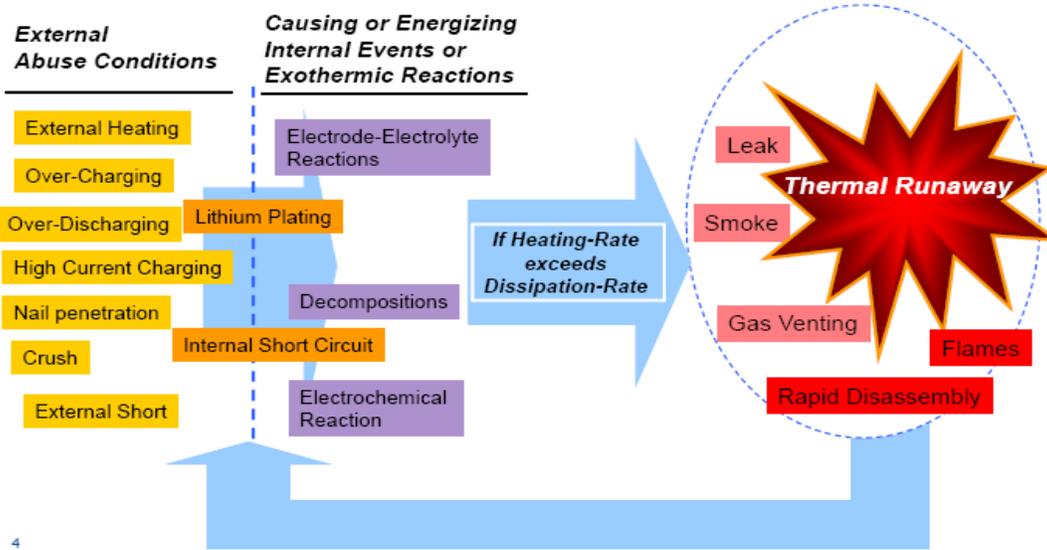


Figure 3. Thermal Runaway Triggers²

The goal of cell and pack designers is to address the various abuse scenarios as well as the consequences of exposure to those scenarios.

Figure 4 indicates safety measures that are being taken on the cell and pack level to protect from abuse conditions.

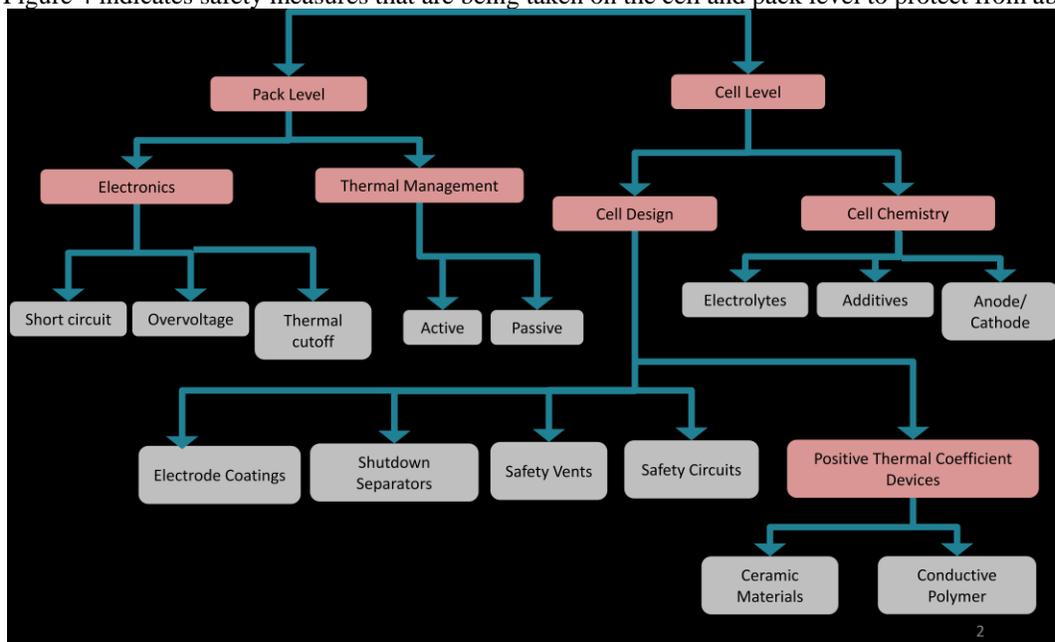


Figure 4. Safety Mechanisms

In spite of the cell level safety mechanisms, the high energy density and presence of oxygen within the battery cell combine to make lithium-ion cells a safety hazard. When a worst case scenario happens, an individual cell can exceed 700°C. As thermal runaway can be triggered by overheating, neighboring cells are in jeopardy when one cell is triggered. The volumetric heat generation (W/m^3) during thermal runaway of single 3.7V, 1.5Ah cell is shown in Figure 5.

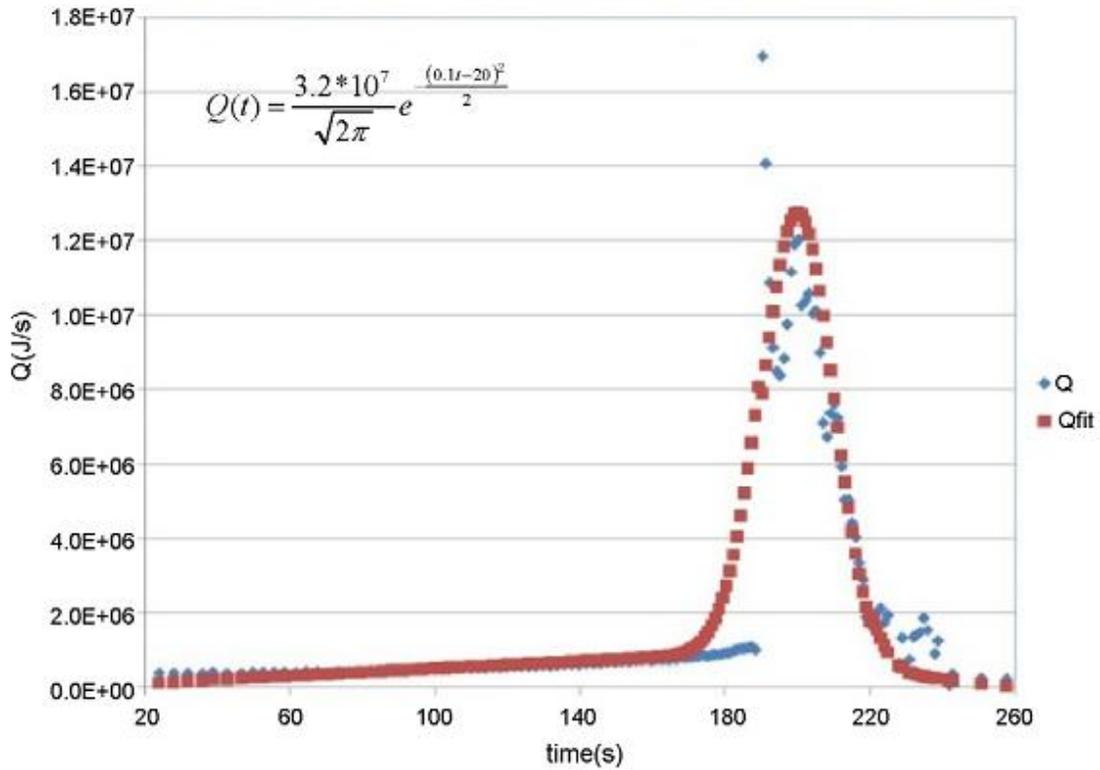


Figure 5. Thermal Runaway Heat Generation³

The pack thermal management system can help prevent a single cell from being triggered or, failing that, it can prevent neighboring cells from being triggered. Single cell catastrophic failure can be prevented if the thermal management system is able to remove heat faster than it is being generated, keeping the cell below the tipping point where the reaction becomes uncontrollable.

If a single cell goes into full thermal runaway the system must be designed to keep neighboring cells from exceeding a safe temperature, which is often in the 95°C range. Figure 6 is an example of failures cascading throughout a battery pack, causing a significant safety risk.

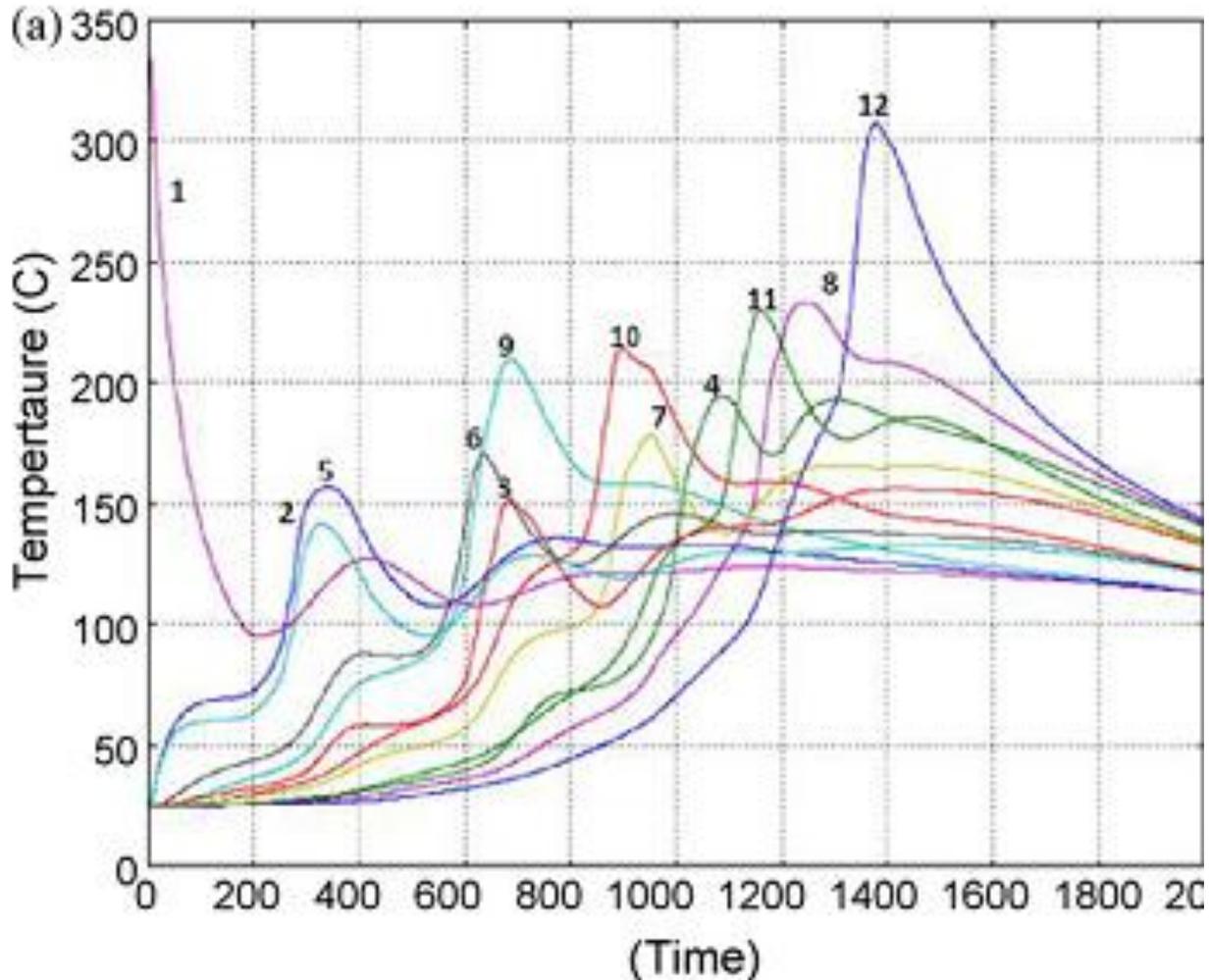


Figure 6. Thermal Runaway Propagation³

Companies have designed liquid, refrigerant and air cooling systems to attempt to prevent cascading failures. These systems are generally effective in ideal environments, but abuse conditions in which the cells are most likely to fail are also conditions where active thermal management that relies on electric fans or pumps may be rendered inoperable. Reports of the Chevy Volt battery fire following a crash test indicate that the liquid cooling system may actually be to blame for the fire. Fisker recalled its Karma PHEV due to a potential fire hazard caused by A123's liquid cooling system.

A truly effective solution must be able to provide thermal management even if the electronic system is disabled. While at the Illinois Institute of Technology, Professors Said Al-Hallaj and J. Robert Selman developed a phase change material approach to battery thermal management that has been shown to solve this issue. A phase change material (PCM) can absorb a high amount of heat in a very narrow temperature band. Water for instance absorbs the same amount of heat when going from ice-liquid phase at 0°C as it does when increasing from 0 to 79°C. If the temperature of that heat absorption can align with the necessary temperature to control a thermal event in a battery, then that material can significantly decrease the temperature of the individual cell and neighboring cells. Paraffins and ester PCM's that meet this criterion exist and are produced commercially for various applications.

Phase change material

As with water, paraffin and ester PCM's, which have the consistency of wax, absorb high amounts of heat in a narrow temperature band while transitioning from solid to liquid phase. Figure 7 shows how systems with and without phase change material behave as the system enthalpy increases.

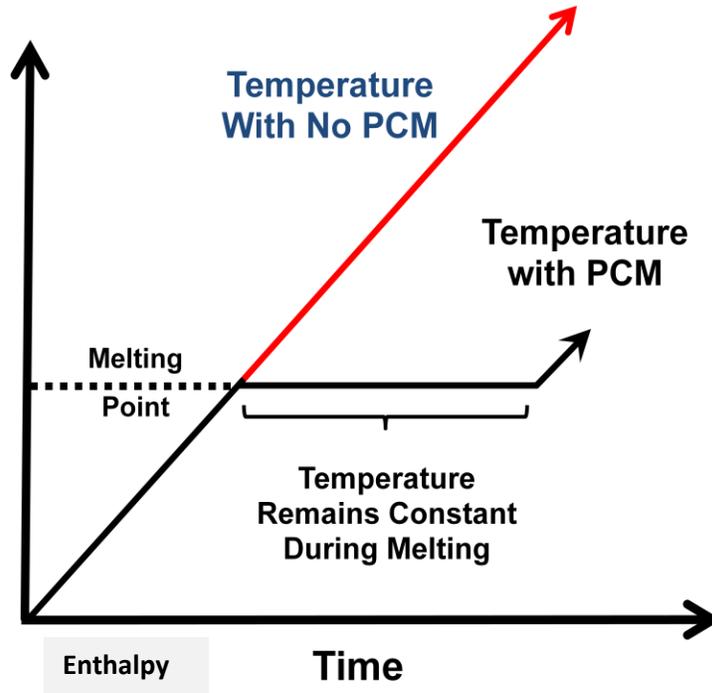


Figure 7. Phase Change Material Diagram

In concept, this approach is a promising solution, but it is driven by the amount of thermal mass available. The amount of thermal mass available is dictated both by the thermal mass in the system and the ability of the heat to access that mass. To enhance the ability of the cell heat to access all of the thermal mass, the PCM can be encased in a thermally conductive graphite matrix. This allows the heat to be conducted to areas of the battery pack remote from the heat generation source, providing maximum benefit.

The ability of PCM-graphite to isolate single cell failure is shown in Figure 8. One simulation is a battery pack with no thermal management while the other unit has a PCM-graphite composite between cells. In the unprotected pack, the entire battery pack is triggered into thermal runaway while the PCM is able to quickly dissipate the heat without further incident.

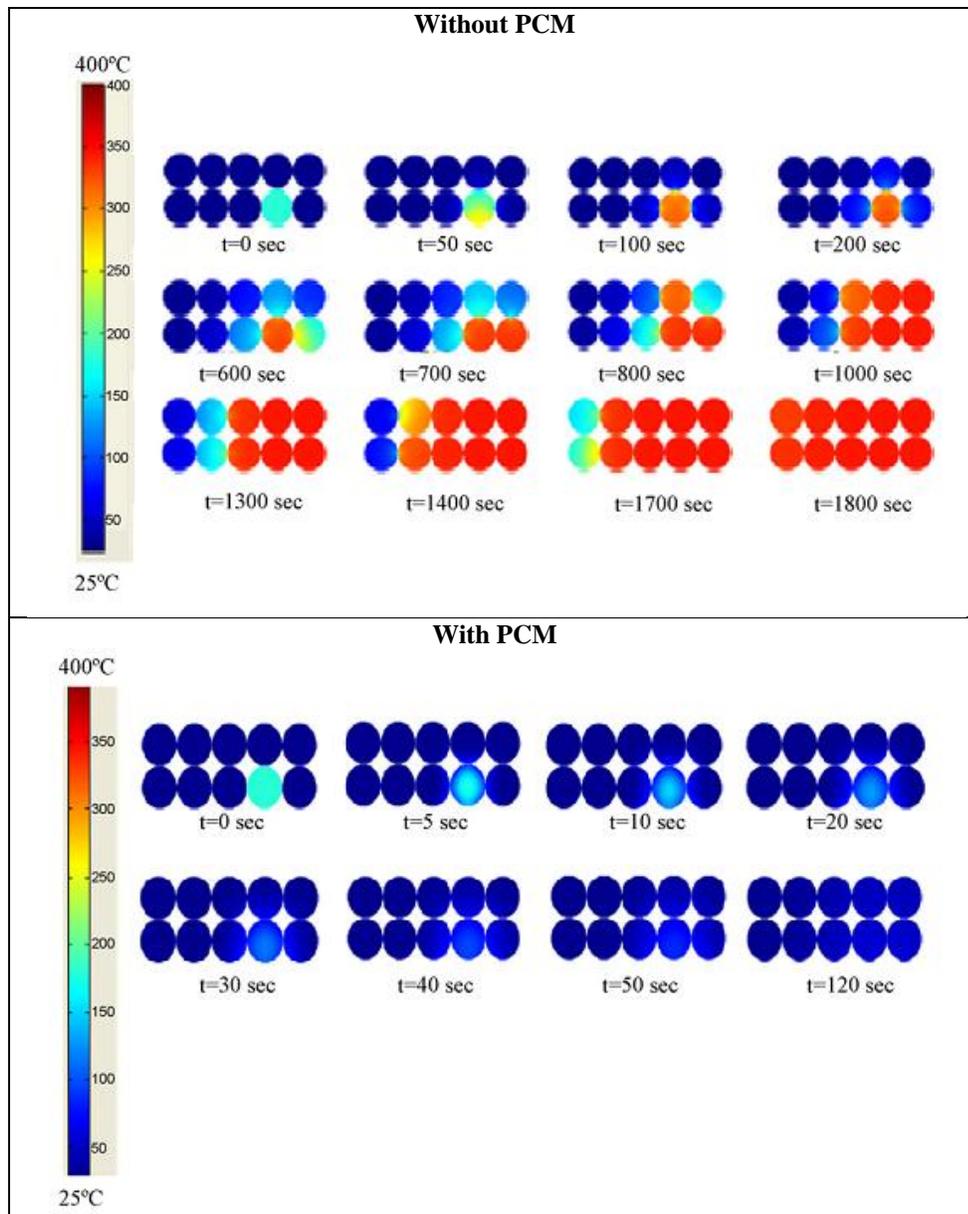
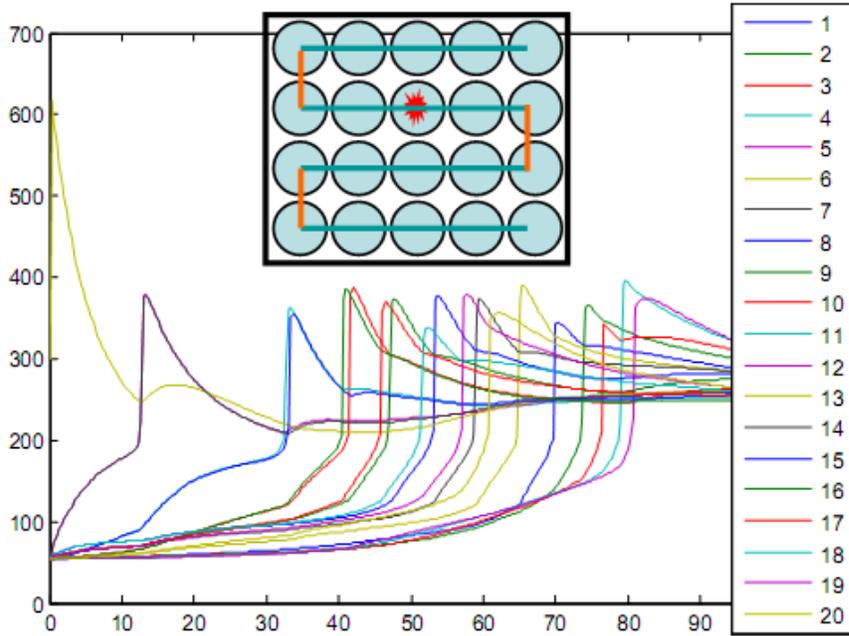


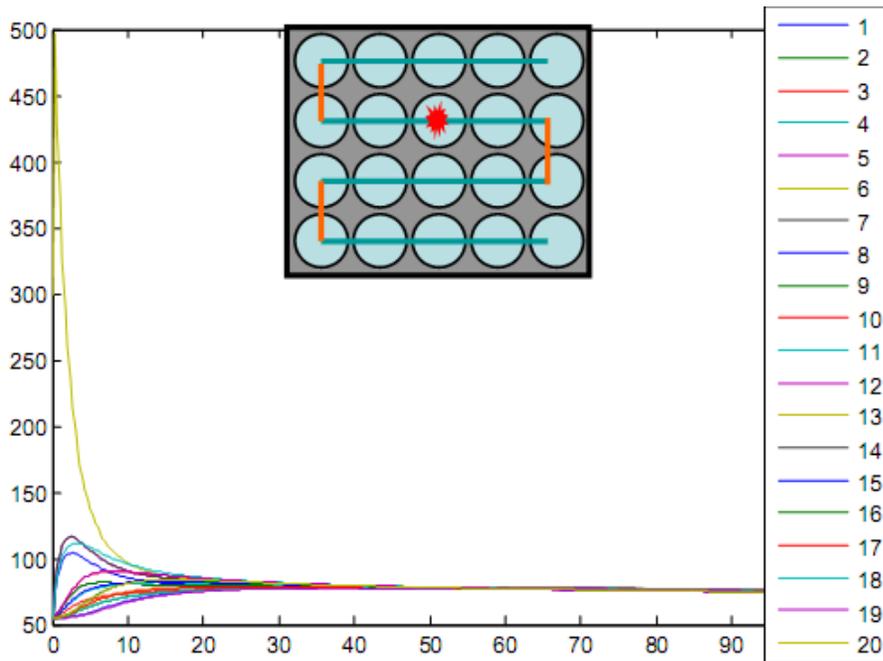
Figure 8. Thermal Runaway Modeling3

This case represents one specific failure scenario and does not reflect the variety of factors that influence the full system design. As discussed, the three important factors are rate of heat generation, thermal mass available, and the ability to access that mass.

The National Renewable Energy Laboratory performed similar modeling on a slightly different battery pack. Results are shown in Figure 9 confirming the comparison of PCM-graphite versus air cooling.



Base case (air)



Graphite matrix impregnated with PCM

Figure 9. NREL Thermal Runaway Modeling2

In addition to modeling work, extensive testing on a battery module level has been performed by the Illinois Institute of Technology and AllCell Technologies. The results of the modeling have been validated through the testing. An independent automotive testing laboratory, a top European battery OEM, and a top European automotive OEM have also separately performed testing that validates the modeling results. Due to confidentiality agreements, those results cannot be shared publicly at this time.

An alternate scenario to the system shown in Figure 8 is if the system has just completed a full discharge in a warm environment and a cell in one corner of the battery pack goes into thermal runaway. Since the pack has just undergone a full discharge, it is possible that a portion of the PCM is already in liquid phase, reducing the available thermal mass; however, the ability of the cell to release heat is also diminished at the end of discharge due to multiple factors.

The difference between the thermal runaway potential and consequences of a fully charged lithium-ion cell and a fully discharged lithium-ion cell is significant. A fully discharged cell is less likely to go into temperature triggered thermal runaway as the lower energy potential within the cell raises the trigger temperature. The rate of heat release is also diminished, reducing the rate that the thermal management system must remove heat. If the cell does end up combusting, the same amount of heat will be released regardless of the state of charge.

The ability to balance out the heat generation and available thermal mass is a matter of specific battery design, but the PCM-graphite gives battery designers a valuable tool in providing a safer battery.

Conclusions

A comparison of lithium-ion versus lead acid was made to exhibit the technical and economic pros and cons of the two systems. A key differentiator in many applications is the lower volatility provided by lead acid systems. To address the risk of combustion in lithium-ion, a phase change material-graphite matrix has been developed to remove heat from an abused cell. The composite material has shown the ability to prevent neighboring cells from being triggered into thermal runaway if a single cell is triggered. The value of this approach was validated through computer simulation and abuse testing of battery packs.

¹ Al-Hallaj S, Selman J. Thermal modeling of secondary lithium batteries of electric vehicle/hybrid electric vehicle applications. *J Power Sources*. 2002; 110: 341-348.

² Pesaran A, Kim G.H, Smith K. Thermal Abuse Modeling of Li-Ion Cells and Propagation in Modules. Presented at AABC 2008..

³ Kizilel R, Sabbah R, Selman J, Al-Hallaj S. An alternative cooling system to enhance the safety of Li-ion battery packs. *J Power Sources*. 2009; 194: 1105-1112.