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Sensor Enhanced and Model Validated Life Extension of Li-Ion Batteries for Energy Storage

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EXECUTIVE SUMMARY

Fro m 2012-2015 DNV GL conducted and managed an ARPA-e[1] funded program under the AMPED[2] technical scope titled "Sensor Enhanced and Model Validated Life Extension of Li-Ion Batteries for Energy Storage". This program investigated the use of off-gas monitoring with chemiresitive sensors developed by NexTech Materials as an added control function for Beckett Energy Systems energy storage products. Through the course of the program, DNV GL performed testing of Li-ion cells (both pouch and cylindrical) under a broad range of conditions including cycling within the manufacturer specification for the cells, cycling at the limit and beyond the recommended C-rate and voltage limits, cycling above the recommended temperature limits, and full overcharge and overtemperature up to and beyond the thermal runaway limit. A number of novel discoveries about the offgassing behaviors of Li-ion batteries were uncovered:

- Despite common industry assertions that offgassing will not occur unless the battery is undergoing thermal runaway, it was found that offgassing does indeed occur during cycling conditions and is an indication that breached cells can function while providing no other indication that their health or life is in jeopardy
- It was found that prior to thermal runaway, batteries can emit low levels of detectable offgassing which serves as an early warning that thermal runaway is about to occur. This early warning was observed under a wide range of conditions and the duration of early warning ranges from as long as 20 minutes and averaged about 7 minutes before the event. This signal preceded voltage or temperature excursions by 2-7 minutes.
- The sensor signal can be converted to binary using moving averages and a technique similar to Bollinger Bands, a technical indicator in stock price technical analysis. Variation of the length of the moving average and the number of standard deviations of movement of the signal can be used to "tune" the sensitivity of the binary signal.
- The repeatability of the signal is dependent on outside influencing factors (such as temperature) though through the program the control circuitry was advanced to include temperature correction factors which increased the reliability of the signal. With these advancements the signal processing was improved and repeatable early warning signals were generated in triplicate and beyond.
- The sensors could be incorporated into the Beckett system with 1-3 units. The binary output can be used for automatic shutdown and/or fire extinguisher control signals and may be also used for maintenance warnings.

These combined benefits provided by off gas monitoring create an opportunity for enhanced control and reduced cost. Early warning provides a means to extend the operational limits of the battery and enable monetization of high value but otherwise "abusive" services, such as occasional high power discharges or low depths of discharge. In addition, life extension beyond the industry-standard 80% capacity is possible, thus extending revenue. In addition, pathways to reduce redundancy in other sensors (such as voltage and temperature) are possible which may reduce the overall system cost.

[1] Advanced Research Projects Agency - Energy
[2] Advanced Monitoring and Protection of Energy Storage Devices

Battery system control legacies extend back to common practices in power system electronics, uninterruptible power supplies, and inverter architectures. It has been estimated that the balance of systems in controls for energy storage systems (ESS) roughly doubles the cost of the batteries alone. While battery system costs have been dropping rapidly from $1000-$1,200/kWh in 2008 to less than $500/kWh today, there are innovations required to reduce the balance of system (BOS) cost in order to reduce the overall cost. Off gas monitoring offers on such potential solution because it provides diagnostics for failing cells, an early warning mechanism for potential catastrophic battery failures, and complements the existing monitoring metrics such as voltage and temperature which can potentially reduce their quantity and cost.

Battery off gases are mainly solvents for the electrolyte which are typically in the ethylene carbonate (EC) family. These volatile organics are detectable by a chemi-resistive sensor which decreases in resistance in the presence of these species. The configuration of the sensor is shown in Figure 1. The chemi-resistive element is contained in a sensor head, and the signal is highly sensitive down to the ppb level. A drop in sensor element resistance is an indication of ethylene carbonate (and related) species detection. In Figure 2 it is shown that the sensor is sensitive to not only EC, but DEC and MEC as well.

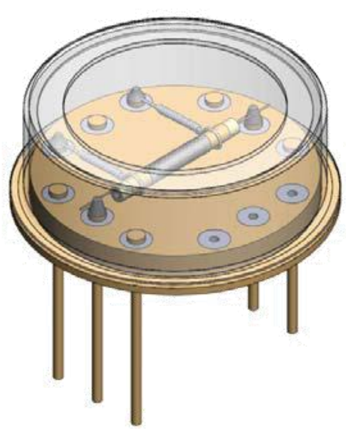


FIGURE 1 **CONFIGURATION OF SENSING ELEMENT.**

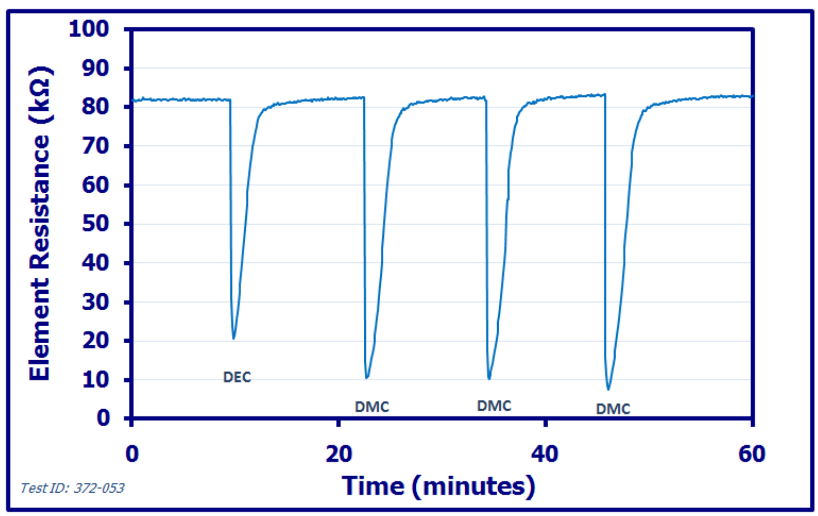


FIGURE 2 **OFF GAS SENSOR ANALOG OUTPUT AS A RESULT OF GAS DETECTION.**

Over 100+ tests were performed in various conditions. The general findings from these tests (Figure 11) indicate that longer duration and low concentration signals from the sensor typically corresponded to non catastrophic or low leak conditions in the cell, while fast, high concentration signals corresponded to imminent or already occurring catastrophic failure.

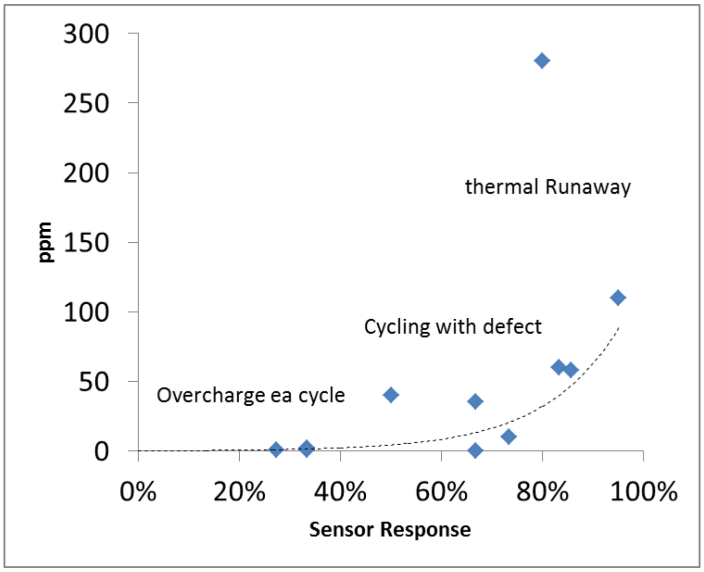


FIGURE 3 **SENSOR RESPONSE AS A FUNCTION OF CONCENTRATION OF OFF GASES IN DETECTION ENVIRONMENT AND THE CONDITIONS WHICH REPLICATE SUCH CONCENTRATIONS.**

The differences in time scales and concentrations are shown in Figure 3. In Figure 4 it is shown that under excessive C-rate cycling, a slow buildup of off gas is confirmed with gas chromatography and an increasing change in the sensor signal was detectable in an enclosed environment. The cell capacity degraded and the off gas concentration increased as time went on. A similar result was confirmed with overcharging each cycle.

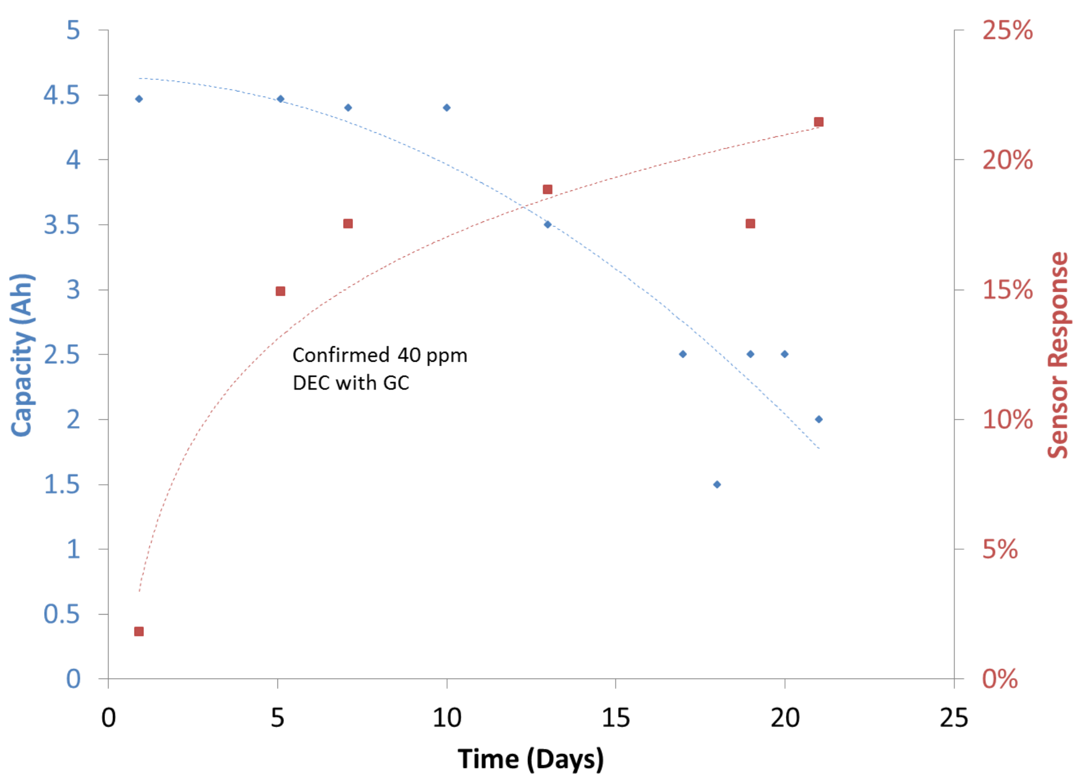


FIGURE 4 **RESPONSE OF SENSOR TO A LI-ION BATTERY CYCLED AT ELEVATED CHARGE/DISCHARGE RATES WITHIN AN ENCLOSURE.**

SENSOR SIGNAL ANALYSIS

Bollinger Band analysis is a technique borrowed from stock market trading. Having evolved from the concept of trading bands, Bollinger Bands can be used to measure the "highness" or "lowness" of the price relative to previous trades. By analogy, Bollinger Bands can be used to measure the "highness" or "lowness" of the NexTech sensor resistance relative to previous environmental conditions.

In stock analysis, Bollinger Bands are very useful for detecting sudden price movements in stocks, for example, a poor performing quarter is announced and the price drops because of a sell-off. When the lower Bollinger Band is crossed, the stock is "oversold". For slow movements, the moving average tracks the price movement, and the oversold threshold may continuously drop below the price and the oversold condition may not be met. By analogy, the "oversold" condition for the off gas signal is interpreted as an off gas event, which is generally sudden. There are additional temperature considerations. Early testing in the program exhibited high sensitivity to temperature. For gradual decreases in resistance (such as temperature drift), the lower Bollinger threshold may not trigger a detection. Thus this method is capable of determining the difference between sudden environmental changes vs. gradual environmental changes.

The Bollinger Band calculation relies upon a moving average of the data or signal, and creates bands above and below that signal that are multiples of the moving average standard deviation. More specifically, these parameters are required:

- an n-period moving average (MA) of the data or signal
- an upper band at k times an n-period standard deviation above the moving average (MA + $k\sigma$)
- a lower band at k times an n-period standard deviation below the moving average (MA − $k\sigma$)

The default choice for the average is a simple moving average, but other types of averages can be employed as needed. In the analysis of the Nextech sensor offgas signal, the departure is generally "downward", i.e., the resistance drops when off gas is detected. Thus the lower Bollinger Band is more relevant than the upper.

An example of the Bollinger Band method is shown below in Figure 5. This test is a pouch cell, overcharged at 20^{o}C. The test variables for this are the number of points in the moving average (n) and the multiple of the standard deviation. It can be seen that n = 100 and k = 2 provides the earliest warning for an event. Similarly in Figure 6 n=100 and k = 2 provides better warning than n = 100 and k = 3. In Figure 7, again n = 100 and k = 2 provides better early warning, even when the sensor signal may be questionable to the human eye, than other conditions.

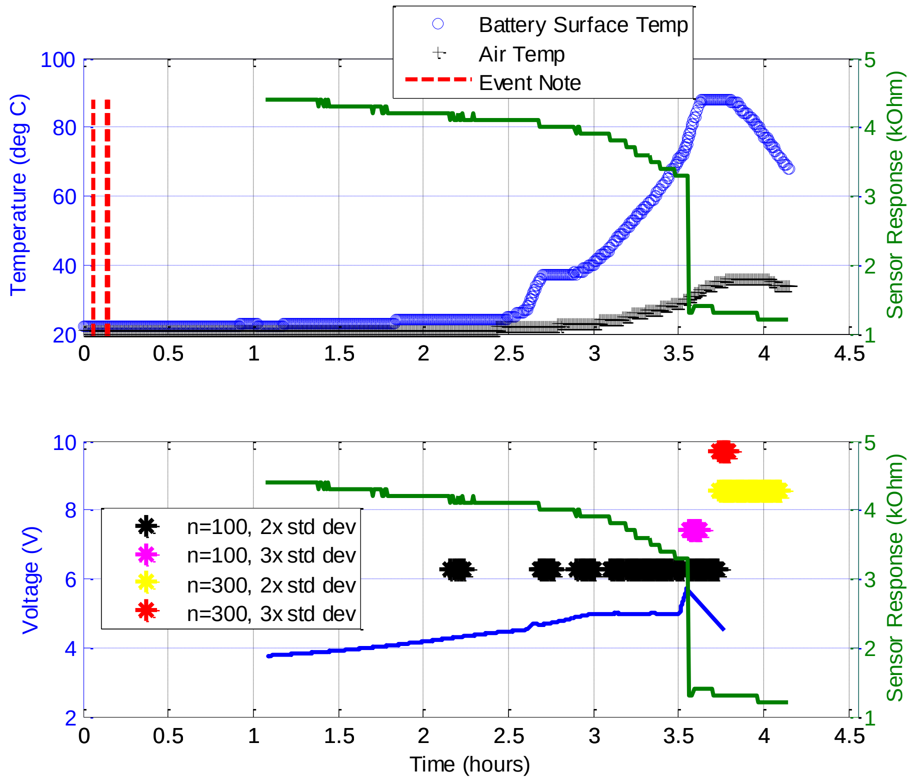


FIGURE 5 **BOLLINGER BAND ANALYSIS OF SENSOR SIGNAL FOR AN OVERCHARGE TEST ON A POUCH CELL.**

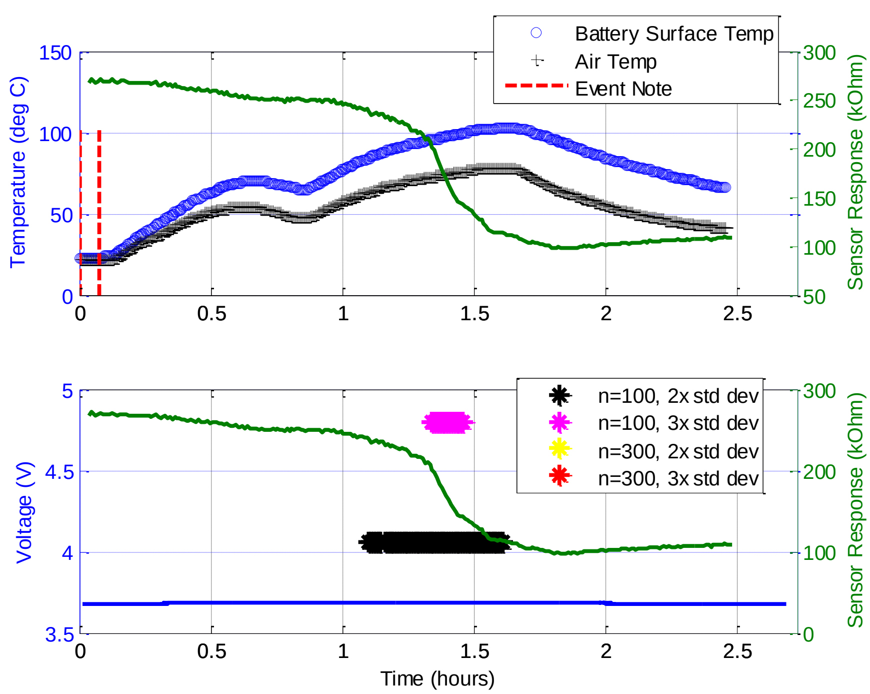


FIGURE 6 **BOLLINGER BAND ANALYSIS FOR POUCH CELL OVERCHARGE AT 120°C.**

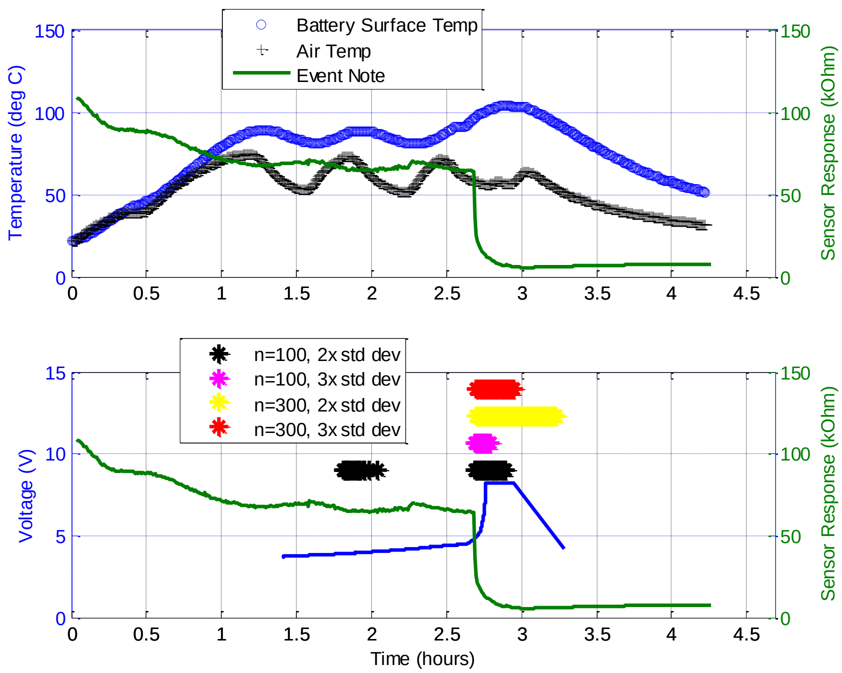


FIGURE 7 **BOLLINGER BAND ANALYSIS FOR OVERCHARGE POUCH CELL AT 100ºC.**

From these analyses, it is apparent that n=100, k=2 may be an alarm condition threshold, with n=100, k=3 as an action threshold. To add greater certainty, a short time frame between crossing the k=2 and k=3 thresholds may be used as a action signal, i.e. system shut down and the actuation of fire control systems or emergency cooling systems. The control methodology has greater success for confirmed thermal runaway or deflagration events. It has some success for subtle or benign offgassing, characterized by intermittent signals throughout the testing. However, some false positives in this case can be attributed to sensor signal drift (often correlated to temperature). Nextech's recent temperature correction measures will greatly improve the detection ratio (confirmed positives). A summary of the test program is shown in the Appendix.

REDUCTION IN FALSE POSITIVES IN BOLLINGER ANALYSIS

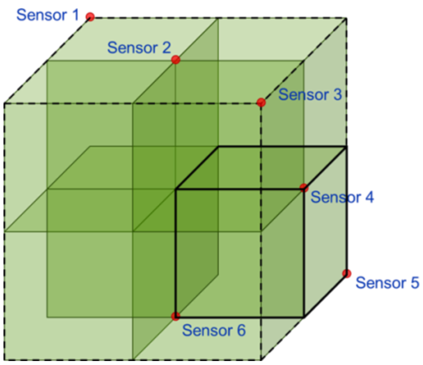
When the Bollinger method is applied it provides a systematic methodology for evaluating the signal. For thermal events and catastrophic failures, the resistance change is highly discernible and the Bollinger analysis reliably identified all GC confirmed events. However batch-batch variation of sensor sensitivity requires tuning of the n and k parameters for that batch, i.e., continued incremental development will refine and provide consistency in the n and k parameters. For the CES system, it was determined that three sensors would be adequate to detect a single offgassing cell (see Q5 report and Figure 8). These calculations are specific to the geometry of the CES system, which is relatively simple and contains 1,920 cells within a cubic meter.

There are several general metrics that can be calculated from this demonstration:

a. Three sensors for 25 kW is 0.12 sensors per kW.
b. Three sensors for 10 modules is 3.3 modules per sensor.

- c. At 192 cells per module, this corresponds to one sensor for every 633 cells.
- d. Finally, this is 3 sensors per cubic meter of close packed cells.

The packing and module geometry will have a high impact on the sensor quantity and configuration.



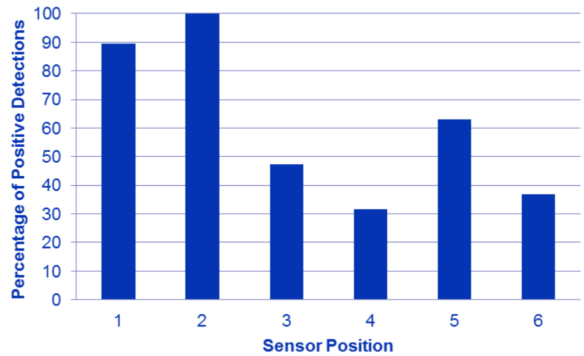


FIGURE 8 **SYMMETRICAL TESTING CONFIGURATION IN THE CES UNIT (LEFT) USED TO DETERMINE OPTIMUM SENSOR PLACEMENT THE TOP SENSORS DISPLAYED THE MOST ACTIVITY ON AVERAGE (RIGHT).**

In the CES study, the three sensors were aligned along the central axis of the battery system. The top most sensor was most active during testing, indicating that in the ambient, room temperature conditions with no airflow, the off gas tended to rise within the enclosure. Thus sensor locations near the top of an enclosure are likely to be effective.

If the system has air movement, sensors at the intake or exhaust of the air channels would likely be effective, however too much volume of air movement will wash out the sensor signal. Slow air movement will make the sensor more effective.

Lastly, a general rule of thumb under ambient conditions is to place the sensors near the center of mass of a battery array.

HOW MUCH OFFGAS CAN COME FROM A CELL?

Anywhere between 5-50 g of electrolyte solvents may be emitted from a 93 g semi-cylindrical cell, which ranges from 5-50% of the cell's mass. In addition, from our testing, we found several benchmark quantities to reference for this testing:

1. Measured concentration from benign offgassing during cell level bench testing: 40 ppm
2. Measured concentration from injection apparatus in DESS unit with good sensor response: 0.44 ppm
3. Expected concentration from a single cell in the DESS unit: 5 – 50 ppm

The sensor has shown good response at < 1 ppm in the DESS injection tests and repeatable responses at the 40 ppm level during bench tests. In very controlled environments, the sensor is sensitive at the 50 ppb level. However, the stability of the surrounding environment and the rate at which the cell is offgassing can alter the detection behavior. As is shown in Figure 9, if we choose a realistic lower limit detection threshold in uncontrolled (but static) environments between 0.01 -

0.1 ppm, detection is feasible within a 16 hours for a cell that contains only 5% electrolyte by mass emitting at 0.01 g/min. Admittedly, the detection behavior will be dominated by the proximity of the sensor to the offgassing battery and inhomogeneity of the mixture within the DESS free volume.

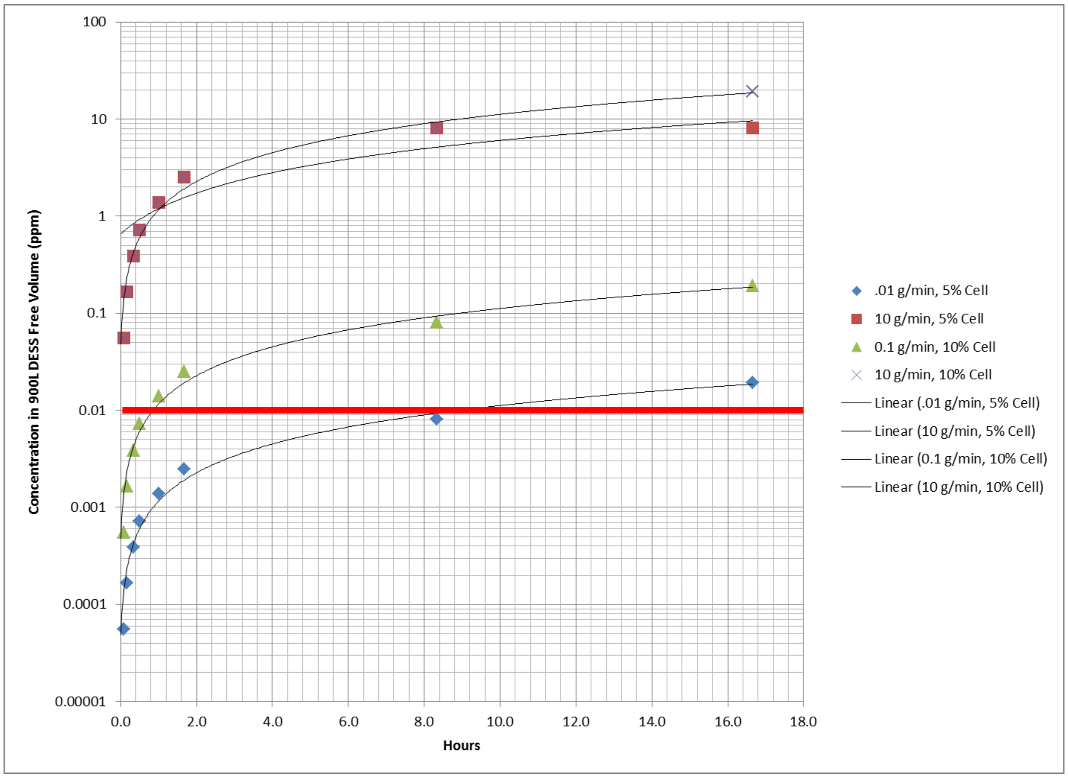


FIGURE 9 **ESTIMATION OF CONCENTRATION GRADIENTS AS A FUNCTION OF CELL EMISSION RATES AND MAXIMUM ELECTROLYTE MASS IN THE BATTERY CELL.**

HOW FAST CAN THE SENSOR DETECT OFF GAS?

With close proximity and rapid ejection of cell contents, the sensor detects the event nearly instantaneously as shown in results such as Figure 7.

In early simulations of offgassing shown in Figure 9, it was found that sensors would see benign offgassing within a minimum of 2 or more hours of injection and as much as 16 hours. Thus, detection could be obtained within a day. For higher level (still benign) offgassing, detection could occur within an hour. The volume of electrolyte solvent released, the volume of the container, the proximity of the sensor to the cell, the sensitivity of the sensor, and air movement within the volume can significantly change these parameters. Near instantaneous detection of offgassing is possible with close proximity and violent discharge of cell contents.

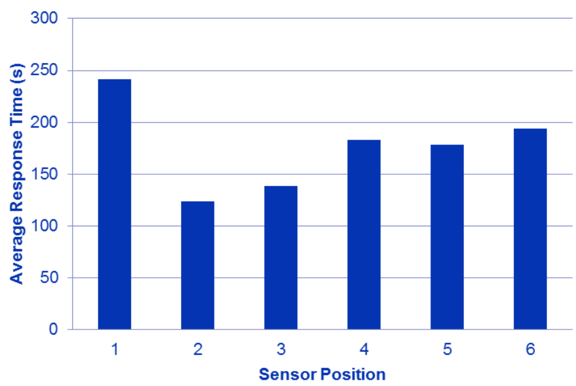


FIGURE 10 **AVERAGE RESPONSE TIME FOR SENSORS IN THE CES SENSOR ARRAY TESTS.**

RECOMMENDATIONS FOR IMPLEMENTING OFF GAS MONITORING FOR ESS CONTROLS

The raw data output is a resistance reading. The most rudimentary control would be a binary output that can be read as "Yes/No" (0 or 1) to offgas. Decisions that can be made from a binary signal are:

1. Emergency alarm
2. Maintenance alarm
3. Shutoff
4. Safety control, such as fire extinguishing or cooling

Additional levels of control can be added, such as

a) 1st threshold = warning alarm
b) 2nd threshold = safety controls and/or shut down

It has been demonstrated that algorithms within the sensor hardware to monitor the moving average of the signal and execute triggers for binary output based on deviation from the moving average are possible. Overall, the range of utility for the sensor spans from minutes (fire prevention) to days (maintenance) as shown in Figure 11.

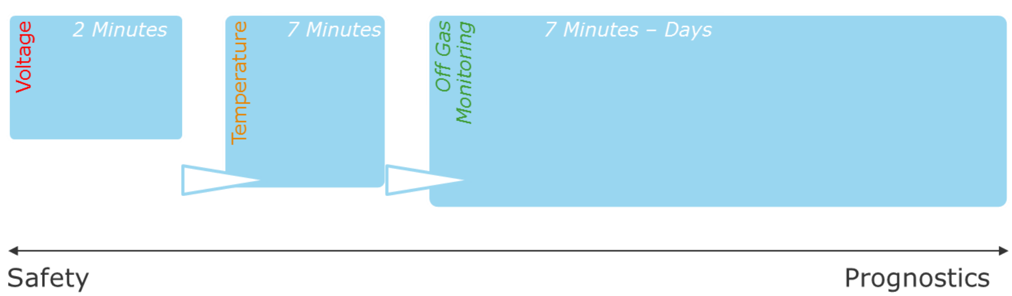


FIGURE 11 **WHILE SAFETY CONTROL IMPLICATIONS REQUIRE MINUTES OF ACTIONABLE INFORMATION, SLOW, LEAKING OFFGASSING CAN PROVIDE DAYS OF EARLY WARNING AN PROGNOSTICS FOR ADVANCED MAINTENANCE.**

The off gas sensor enables differentiation of signals for imminent failure or actionable data. The logic is as follows (Figure 12). The off gas sensor adds an additional barrier level in the event tree and also creates a new decision pathway to enable Class D extinguisher activation.

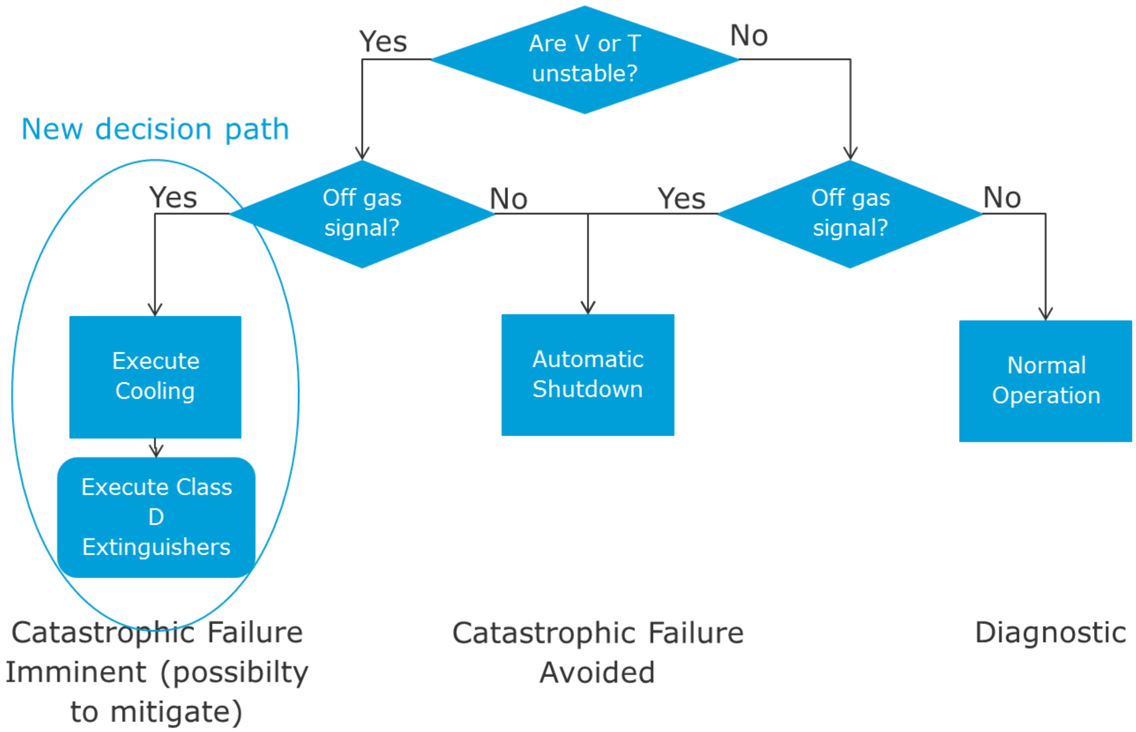


FIGURE 12 **NEW DECISION PATH AND SAFETY LEVEL CREATED WITH THE ABILITY TO SENSE OFF GAS.**

FIRE SAFETY AND EARLY WARNING OF THERMAL RUNAWAY WITH OFF GAS MONITORING

Some newsworthy failure events for batteries have left a bad mark on the industry which has hindered growth. The reasons for those failures were often external to the technology itself, but the battery has borne the burden of guilt. Part of the reason for this is the nature of the social phenomena of anchoring and confirmation bias. Anchoring is the practice of rigidly adhering to ideas of the past with an unwillingness to adopt new ideas. Confirmation bias is human nature to actively seek data, even false data, to support an anchored belief. Thus when old incidents of outdated technology left the impression that batteries had safety issues, the idea anchor was established, and every event that follows reinforces this anchored belief with confirmation bias. In many cases the eagerness to assign an unsafe label to batteries is unqualified and the reasons for this are outlined below.

At its core, every battery system has the same elements: a single cylindrical or pouch cell is scaled into stackable modules which may have basic control and intelligence, which are then integrated into larger systems which have an overall control and intelligence architecture, which is connected to external control and communication to connect it to the larger network (grid, microgrid, automotive electronics system, ship power system, etc). The typical architecture is shown in Figure 13. All of this hardware integration detail is usually obscured by the system containment which is usually a metal enclosure such as an IP-rated metal box or a shipping container. There can be minor omissions in the architecture that may seem acceptable from a design standpoint, but it is often these omissions that add complications to safety incidents. These omissions are most commonly: improper or missing cell containment to prevent thermal runaway cascading, lack of monitoring at a sub-module or cell level, error in the BMS leading to battery operation outside the recommended voltages or temperature specs, and – most commonly – third party damage.

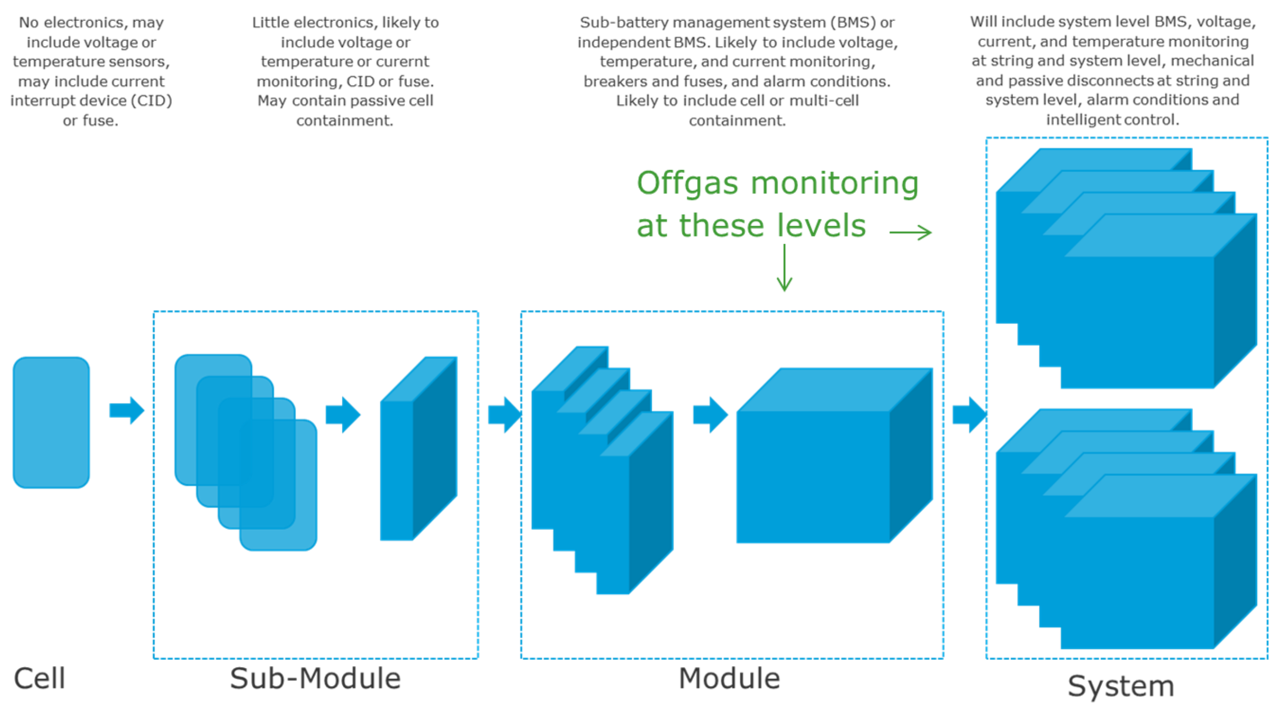


FIGURE 13 **TYPICAL BATTERY SYSTEM ARCHITECTURE.**

Unfortunately, when a vehicle encounters a rare situation that causes it to catch on fire, or an airplane is grounded due to battery thermal runaway, the general public sees such an event on the news and reinforces the anchored beliefs concerning safety with confirmation bias, despite the fact that the extenuating circumstances that led to those incidents may have been extraordinary or in some cases, unfortunate and uncontrollable events. As shown in the figure, the complexity of the battery system depends on the level of redundant safety barriers all the way down to the cell level, but a design flaw at any of these levels can cause a system-level problem.

While this hardware and physical package looks analogous across industries, the environments where these systems are deployed are highly disparate, and therefore the hazards the batteries may encounter have different probabilities of occurring; it is the probability, not the hazard, that matters. When a failure occurs, in hindsight it may be easy to see the system architecture and ask why certain barriers weren't in place. But the perceived probability of the hazard and the impact on system cost to mitigate it will determine whether the mitigation barrier is incorporated into the final design. This is explicitly defined by the Learned Hand Formula, which states that the need for mitigation *M* is the product of potential liability I and the probability I of the liability, i.e. $M = PL$. In modern practice, the act of quantitative risk assessment is similar, i.e.,

$$Risk = Probability * Consequence$$

This is exactly what occurred with the airline case.[3] The need for cell containment and separation was not as well understood in 2007[4] - when the design was type approved with special conditions and frozen - as it is today. The special conditions mandated that the design preclude explosion and the occurrence of self-sustaining, uncontrolled increases in temperature or pressure. The design considerations also mandated that no explosive or toxic gases or corrosive fluids shall accumulated or damage nearby equipment. Of the nine special conditions listed, all of which clearly acknowledged the risk of offgassing and thermal runaway, none of them mentioned cascading or fire extinguishing measures. At that time, there was obviously the probability of a single cell defect leading to cascading thermal runaway, and the consequence of such an event grounding an entire fleet seemed so out of reach that it is obvious why cell separation was not included in the design. By the time the APU made it through all of the FAA approvals and began service, the automotive industry had already learned that lesson and the stationary industry was closely following. Yet today, the regulatory framework is only explicit about certification to UN 38.3 which contains within it 8 basic abuse mechanisms which certify whether a battery can be transported. These hazards are:

- Altitude or pressure
- Thermal
- Vibration
- Shock
- External Short Circuit
- Impact
- Overcharge
- Forced Discharge

After passing UN 38.3, a battery manufacturer can ship a battery cell or module on land, sea, or air, because it is believed that these tests are comprehensive enough to evaluate everything a battery might encounter in infinite hazard situations. While standardized abuse testing has narrowed battery failures down to 8 possible scenarios, the number of combined circumstances that would lead to one of these failure modes are infinite in the real world, and the consequences of such events can vary from zero to very large. And certification to this standard does not address methods to arrest cascading or extinguish fires and provide rapid cooling to halt thermal runaway.

EXTINGUISHING FIRES – A COOLING AND EXTINGUISHING PROBLEM

[3] "Multilevel Forensic and Functional Analysis of the 787 Main APU Lithium Ion Battery" Project 13CA50802. Underwriters Laboratories. May 2014.
[4] Interim Factual Report, National Transportation Safety Board Office of Aviation Safety Washington DC 20594, march 7, 2013. NTSB Case Number DCA13IA037

While electrical safety and interconnection of stationary energy storage systems is an obvious issue, the most mystical seems to be the topic of fire. The scale of batteries is a different level than the automotive sector, i.e. these batteries are megawatt scale, not kilowatt scale. A typical 18650 cylindrical battery can discharge about 8 W for an hour. If these were connected in series to create a megawatt, there would be 119,000 batteries in the unit. The original Tesla Roadster, by comparison, had qty 6,000+ cells in it. [5]Each contained a current interrupt device or internal fuse to prevent thermal runaway at the cell level. Then the electronic controls at the string and system level provided further active and passive means to control safety events.

In the stationary case, the risk of fire is not that the system catches on fire on its own, but becomes the victim of the fire and the local fire department must come to the scene and extinguish it and may encounter dozens if not hundreds of cells on fire. In such a scenario on-board automated extinguishers and cell separation can be overcome by heat and fuel availability external to the system.

A Li-ion battery cathode fire is exothermic hence the term *thermal runaway*, which implies that additional heat is being generated uncontrollably. When a Li-ion battery cathode is being consumed exothermically, it is a metal fire. Metal fires require class D extinguishers which are not frequently encountered by the typical fire fighter. Most local firefighting departments may be more accustomed to structure fires, residential grease fires, fires in commercial buildings or apartment buildings, or more intense situations like fires in a manufacturing facility or refinery. All of those situations typically require Class A, B, C, extinguishers. Water, for example, is a Class A extinguisher. The battery industry hasn't helped things by typically issuing a multi-Class A, B, or C fire extinguisher (like FM200) with their stationary systems while stating to their customers that the system is sufficient to extinguish the fire. To the uninitiated, they are led to think that FM200 is an adequate fire extinguisher for a Li-ion battery despite the fact that it is a metal fire. There is missing information in such a claim. It is not the intention of battery manufacturers to mislead – FM200 can be an adequate extinguisher but only when used at the appropriate time. The true story is that a Li-ion fire *changes class* at it evolves (Figure 14). In the figure, the incipient fire may be an incipient fire in electronics or via a spark, which can fall under Class A, B, or C. Once thermal runaway begins it is a metal fire (Class D). During this time the FM 200 system is not suitable for a metal fire, though it may provide a momentary cooling effect which may be enough for a single cell. But the cathode is consumed quickly (depending on the size of the cell, perhaps within a few minutes) and once that exothermic fuel is consumed the remaining plastic packaging and polymer separator and binders from the battery continue to burn, at which point it is no longer a metal fire and it devolves back to a Class A, B, or C fire at which point FM200 is a sufficient extinguisher. In fact, when DNV GL conducts Li-ion abuse tests in its own labs, our procedure is to stand by while the cathode burns and when heat has died down to sufficient levels, we put out the fire with a CO_2 extinguisher.

Class D extinguishers like copper metal powder or sodium chloride are less practical for automated extinguishing, but brominated hydrocarbons in a gel form using hydrophilic surfactants and a film forming fluorocarbon[6] can be packaged in similar ways as gases. The state of the art in extinguishing the Li-ion fire is to contain the fire and suppress the heat, which is why the NHTSA

[5] Specifications: Tesla Roadster. Tesla Motors Inc, 2011

[6] US Patent 5833874 A "Fire Extinguishing Gels and Methods of Preparation and Use Thereof". Dec 1995.

has recommended the use of "copious amounts of water"[7] in extinguishing practices. While this may be appropriate for a vehicle, it is less appropriate for a stationary system that is an order of magnitude larger, has different cell containment and cell isolation mechanisms, and the collateral damage associated with excessive water dousing may be costly, unnecessary, and unacceptable. In addition there are concerns about the mix of water with fluorine-based reactants in the Li-ion battery binders that can create toxic byproducts, such as POF_3.

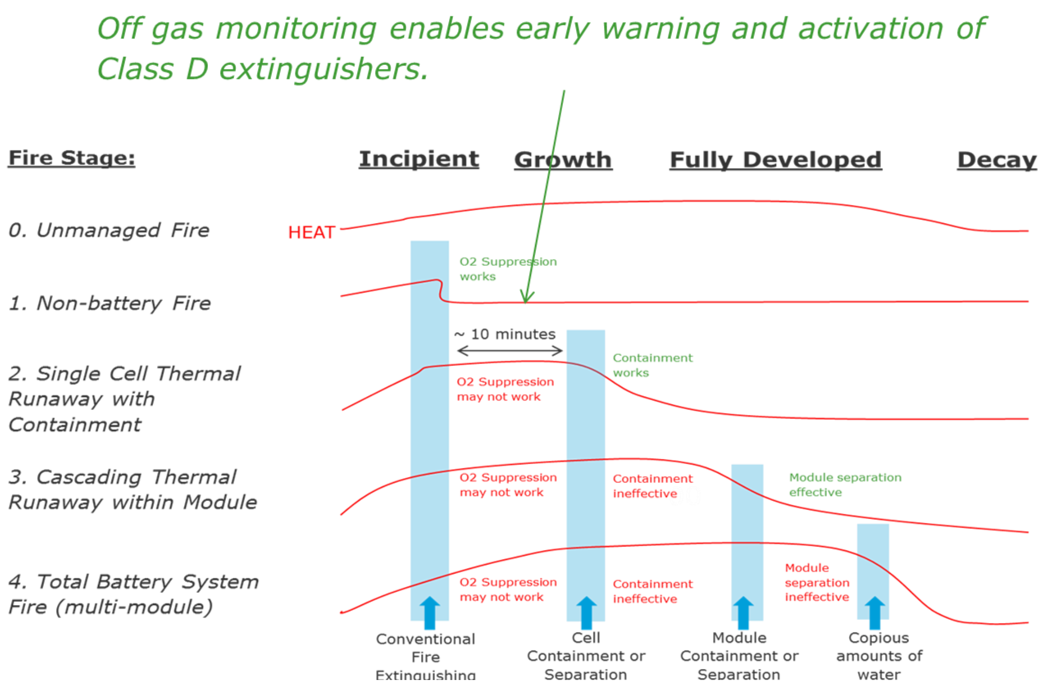


FIGURE 14 **A LI-ION BATTERY FIRE EVOLVES THROUGH DIFFERENT FIRE CLASSES AND IS A CLASS D METAL FIRE DURING THE EXOTHERMIC CONSUMPTION OF THE CATHODE.**

TABLE 1 **COMPARISON OF EXTINGUISHER TYPES AND THEIR APPROPRIATENESS FOR A LI-ION FIRE.**

Suppression System (gas or trade name)	Fire Class	Collateral Damage Risk	Electrical Conductivity	Appropriate for Thermal Runaway?	Thermal conductivity (heat management)	Human Toxicity
DuPont FM200	A,B,C					
CO_2	B, C					
Water (Deionized)	A					
3M Novec 1230	A,B,C					
Copper Powder	D (only lithium)					
Foam	A,B					
Cold Fire	A,B,D					

[7] "Statement of National Highway Traffic Safety Administration on Possible Fires in Li-ion Vehicles Involved in a Crash" Lynda Tran, Friday Nov 11, 2011. Press release.

There are technical solutions to battery system failure modes today. First, cascading thermal runway can be prevented with adequate cell separation and containment, and second, heat can be managed with a number of extinguishing agents, some of which are Class D extinguishers and compliment A, B, or C type extinguishers The missing link is the means to distinguish the fire from a Class D fire or other fire before it happens. This is the role of off gas monitoring. (Table 1) As shown in the table, no single extinguisher is all "green" in the categories listed.

Other relevant categories for extinguisher selection might include whether the extinguishing media is easily adapted to an automated system, or how much cost it may add to the system, whether it requires frequent maintenance or has a limited shelf life, or whether it can be staged or mixed with other class extinguishers.

EARLY WARNING AND CLASS D EXTINGUISHING WITH OFFGAS MONITORING

The value proposition of off gas monitoring is the ability to detect catastrophic failure early. Because the sensor is providing early detection of thermal runaway explicitly, it is a means to prepare and execute Class D fire extinguishing media and mitigate the fire before the threat of cascading arises. As shown in Figure 15, the sensor detects offgassing prior to thermal runaway and provides a means to distinguish imminent catastrophic failure from benign system malfunctions. Across all tests with similar thermal and overcharge failure modes, the sensor provided warning 2 minutes ahead of a voltage change, >7 minutes ahead of temperature excursions, and 7-8 minutes (on average) ahead of the actual thermal runaway event. In some cases, warning was as much as 20 minutes ahead as shown below.

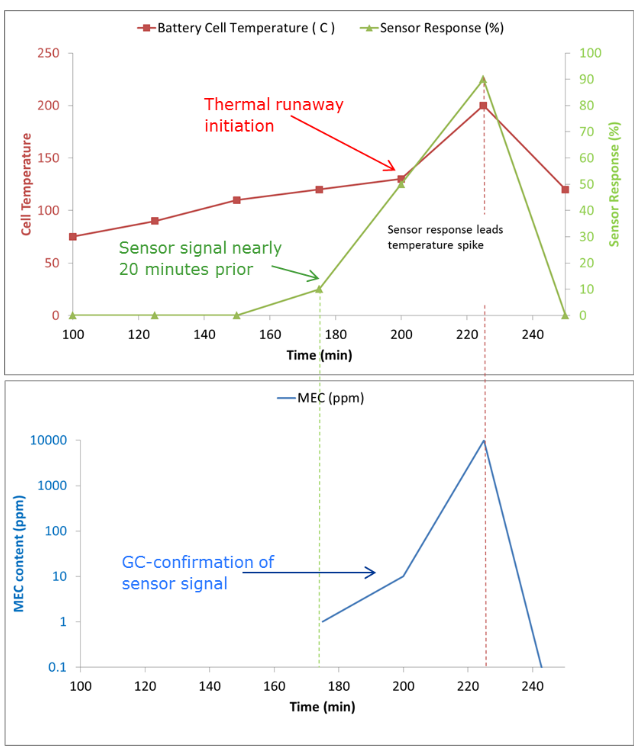


FIGURE 15 **THE SENSOR RESPONSE PRECEDES THERMAL RUNAWAY AND PROVIDES EARLY WARNING, ENABLING THE USE OF STAGED EXTINGUISHERS.**

Such detection capability can be used directly to trigger and execute staged extinguishing strategies for ESS. In the best case, the early warning can enable cooling strategies that may prevent thermal runaway altogether and greatly impact ESS safety overall.

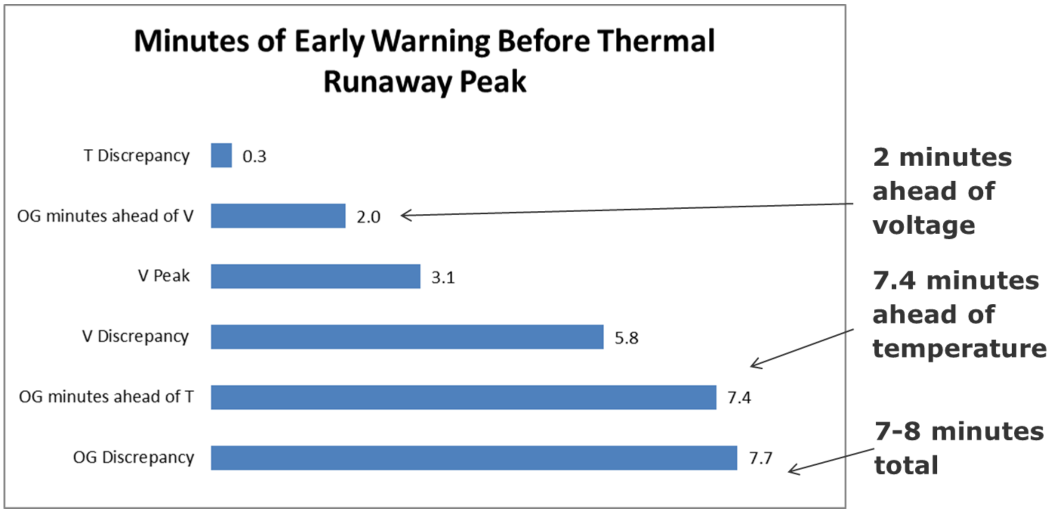


FIGURE 16 **REPEATED TESTS STATISTICALLY HAVE SHOWN ON AVERAGE THAT OG SENSING PRECEDES VOLTAGE WARNINGS UP TO 2 MINUTES EARLY AND ON AVERAGE PROVIDES 7-8 MINUTES OF ACTIONABLE EARLY WARNING.**

ECONOMIC BENEFIT OF ENHANCED SAFETY FOR ESS WITH OFF GAS MONITORING

The sensor can reduce risk associated with safety events. This is hard to quantify, but can be highly valuable. A list of potential value streams and their examples are shown below and is further illustrated in Figure 17.

- Avoidance of Catastrophe
- Life Extension
- Expanded Utilization (Capacity, power, temperature)
- Reduced Capital Cost
- Decreased downtime

These value propositions also depend on the sensor cost. Like all manufacturing, the cost of the sensor is dependent on the production volume. At low volumes, the sensor can be $200-$1000. At high volumes, it can be $100 or less.

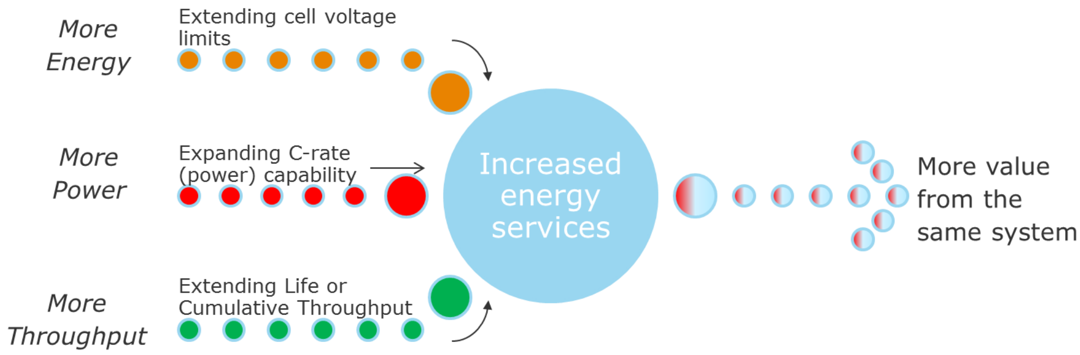


FIGURE 17 **OG MONITORING PROVIDES OPPORTUNITIES FOR EXPANDING THE POWER, ENERGY, OR LIFETIME LIMITS OF ESS.**

In general, an instrumented system offers the following benefits over a system without monitoring or sensor instrumentation (Table 2). The monitored system provides all of the cost reduction opportunities in red.

TABLE 2 **LIFETIME COSTS OF AN ASSET – MONITORED VS. UNMONITORED.**

Non-Instrumented System	Instrumented System
Capital Cost	Capital Cost
+ Inspection Costs	+ Inspection Cost
+ Replacement Costs	+ Replacement Costs
+ Downtime Costs	+ Downtime Costs
+ Maintenance equipment costs	+ Maintenance equipment costs
	- Avoided Inspection Costs
	- Avoided Replacement Costs
	- Avoided Downtime Costs
	- Avoided maintenance equipment costs

To estimate the cost –benefit of a monitoring system, DNV GL has performed a similar analysis for wind turbine blades and used the following inputs to assess the lifetime cost benefit of monitoring:

- System Power
- System Energy
- System capacity factor
- Revenue per MWh
- Componentry Costs
- Downtime per failure
- Equipment costs per failure
- Annual inspection costs
- Failure rates
- Downtime reduction with early detection
- Cost of prevented failures per detection event
- Detection Success Rate
- Cost of monitoring system
- Fraction of actionable faults
- Inspection reduction with use of monitoring

In DNV GL's analysis of SHM systems for wind turbine blades, sensitive cost benefit factors were consistently determined as:

1) Reduction in inspection costs
2) Fraction of actionable faults

For stationary ES systems, inspection costs may not be as high as it is for wind turbines, but the fraction of actionable faults is certainly relevant. See "Catastrophe Avoidance" to understand how detection probability is related to the fraction of actionable faults.

A softer benefit that is more difficult to quantify is the perceived quality and safety of the system. This alone may be enough to command a premium.

CATASTROPHE AVOIDANCE

To avoid a catastrophe, the cost can be estimated as

$$Avoided\ Cost = p_d * \ p_c * C_c \qquad (1)$$

Where p_c is the probability of a catastrophe, p_d is the probability of detection, and C_c is the costs of that catastrophe. This assumes that the detection of the catastrophe is actionable. In Q3, DNV GL demonstrated that this is indeed possible: a pouch cell on the verge of thermal runaway was controlled, pulled back from thermal runaway, and salvaged. Cycling continued for months thereafter, even with a cell breach.

To place some example numbers in this calculation, even if the probability of catastrophe is very low (1%), the probability of detection is reasonably high (60%), the cost can be very high ($3,000,000), and thus the avoided cost is significant ($18,000). If this cost is more than the cost of the sensor system, the investment is justified. The catastrophe cost may include property damage, environmental damage, downtime, and/or loss of life.

LIFE EXTENSION

Life extension may add several useful months or years to the storage asset. It has been stated clearly by the industry that extending the life of the system beyond 80% may pose a safety risk. If the sensor provides some assurance that the system can be operated beyond 80% capacity safely, then additional revenue is possible. This additional revenue is enabled by the sensor system.

Each additional time period of use corresponds to additional revenue, or conversely, additional opportunity to reduce the levelized cost of energy (LCOE) via more kWh delivered. If the revenue potential per kWh is R_{kWh}, and there is the ability to deliver energy at the rate of E_d (kWh/mo), the expected lifetime of a non-sensor equipped system is L (in months), and the potential life extension percentage is L_{ex}, then:

$$Additional\ Revenue = L * R_{kWh} * E_d * (L_{ex}) \qquad (2)$$

If this cost is more than the cost of the sensor system, the cost is justified.

EXPANDED UTILIZATION

In the face of uncertainty, humans tend to err on the side of caution. As battery systems have been developed, a legacy of conservative battery management has evolved because of safety concerns and lifetime anxiety. For example, underutilization of the full state of charge is a standard industry practice. The purpose of this practice is to maximize life and avoid voltage conditions that may be unsafe. To the latter point, most Li-ion batteries that operate within the manufacturer's recommended voltage limits (2.7 – 4.2V, for example, for $LiCoO_2$) are generally not at hazardous voltage conditions, yet a systems integrator may reduce the voltage range even further because of liability concerns - for example within a 2.9 – 4.0 V (cell equivalent) range - which means that the battery has unused capacity and a capital cost burden that must be borne throughout its useful life.

If the sensor provides assurance and reliably enables early warning or enhanced safety actions, greater confidence can be offered if these parameters can be expanded. For example, it may be the case that for opportunistic scenarios, occasional excursions above or below the conservative voltage limits are possible in order to maximize revenue or provide high value services. In (2) we showed the total revenue over the life of the system. Additional revenue opportunities may add to this system revenue, though at a reduction in life or a safety risk. Greater revenue can be generally quantified with these simple terms:

- Life lost per event = L_{loss}
- Revenue from rare event = R_{event}
- Number of rare event = n_{event}
- Overall lifetime frequency of rare events = f_{event}
- Probability of unsafe outcome = p_{unsafe}
- Consequence of unsafe outcome = C_{unsafe}

The enhanced revenue of the system thus has three terms: the reduction in revenue due to the impact of life loss by these events; the revenue earned by these events; and the impact of potentially unsafe outcomes by these events. If the sensor reduces p_{unsafe} to near zero, that term is reduced to near zero.

$$Enhanced\ Revenue = (L - n_{event} * L_{loss}) * R_{kWh} * E_d + n_{event} * R_{event} + f_{event} p_{unsafe} C_{unsafe} \quad (3)$$

In this case if $n_{event} * R_{event}$ is higher than the sum of reduced life revenue, unsafe consequence terms, and added sensor system cost, the use of the sensor system is justified.

CAPITAL COST REDUCTION

If more SOC can be used, there may also be a capital cost reduction benefit by reduction of the overall pack size (and thus quantity of battery cells). If more confidence is provided in the operational temperature range, reduction for cooling systems or hardware may be possible. Similar arguments may be used for current or power capability.

$$\text{Capacity Capital Cost Reduction} = (\text{Baseline Capacity} - \text{Downsized Capacity}) * \frac{\$_{capacity}}{kWh} - \text{Sensor System Cost} \quad (4)$$

OR

$$\text{Cooling Capital Cost Reduction} = (\text{Baseline Cooling} - \text{Downsized Cooling}) * \frac{\$_{cooling}}{kWh} - \text{Sensor System Cost} \quad (5)$$

In these cases, if the capacity or cooling reduction benefit is greater than the sensor system cost, it is justified.

DECREASED DOWNTIME

This methodology has been used to justify investment in sensors for wind turbines for structural health monitoring as shown above. The reduction in downtime cost is a function of the opportunity cost of the downtime. If the sensor system can reduce downtime with proactive maintenance schedules, then it provides a net benefit to the system.

- Average revenue per hour = R_{avg}
- Hours of downtime = t_{down}
- Downtime reduction due to sensing = t_d

$$\text{Downtime Cost Reduction} = \text{Baseline Downtime Cost} - t_d * t_{down} * R_{avg} + \text{Sensor System Cost} \quad (6)$$

If the downtime reduction factor is greater than the sensor system cost, then the investment in sensing is justified.

SUMMARY OF MONETARY BENEFITS FROM MONITORING

Previously it was shown in Table 2 that the baseline system has capital, inspection, replacement, downtime, and maintenance equipment costs (rentals and use fees)[8] associated with its operation. Based on the above analysis, the risk of using the system should be included in the baseline cost. However in the righthand column, the additional benefits of avoided capital costs, additional lifetime revenue, rare event revenue, and risk reductions are possible (added in green). This is shown in Table 3.

TABLE 3 **EXPANSION OF MONITORING BENEFITS.**

Non-Instrumented System	**Instrumented System**
Capital Cost	Capital Cost (including sensors)
+ Inspection Costs	+ Inspection Cost

[8] For a wind turbine, a crane is required to replace a blade or nacelle. This is a very high cost. For an ESS, trucks, manual or hand-operated cranes, or forklifts may be required, which may be a less impactful cost than in the wind turbine case.

+ Replacement Costs	+ Replacement Costs
+ Downtime Costs	+ Downtime Costs
+ Maintenance equipment costs	+ Maintenance equipment costs
+ Risk	- Avoided Inspection Costs
	- Avoided Replacement Costs
	- Avoided Downtime Costs
	- Avoided maintenance equipment costs
	- Avoided capital costs
	+ additional lifetime revenue
	+ rare event revenue
	- Risk reductions

FIGURE 18 **BECAUSE OF THE ADDED SAFETY BENEFIT, THE SENSOR MAY PROVIDE CONFIDENCE TO EXPAND OPERATIONAL LIMITS, THUS ENABLING DOWNSIZING AND LIFE EXTENSION.**

CONCLUSIONS

It was found that while enhancing safety and enabling the use fo Class D automated fire extinguishers, the potential monetization pathways for such sensing include:

- Avoidance of Catastrophe
- Life Extension
- Expanded Utilization (Capacity, power, temperature)
- Reduced Capital Cost
- Decreased downtime

Despite common industry assertions that offgassing will not occur unless the battery is undergoing thermal runaway, it was found that offgassing does indeed occur during cycling conditions and is an indication that breached cells can function while providing no other indication that their health or life is in jeopardy.

It was found that prior to thermal runaway, batteries can emit low levels of detectable offgassing which serves as an early warning that thermal runaway is about to occur. This early warning was observed under a wide range of conditions and the duration of early warning ranges from as long as 20 minutes and averaged about 7 minutes before the event. This signal preceded voltage or temperature excursions by 2-7 minutes.

The sensor signal can be converted to binary using moving averages and a technique similar to Bollinger Bands, a technical indicator in stock price technical analysis. Variation of the length of the moving average and the number of standard deviations of movement of the signal can be used to "tune" the sensitivity of the binary signal.

The repeatability of the signal is dependent on outside influencing factors (such as temperature) though through the program the control circuitry was advanced to include temperature correction factors which increased the reliability of the signal. With these advancements the signal processing was improved and repeatable early warning signals were generated in triplicate and beyond.

The sensors could be incorporated into the Beckett system with 1-3 units and a binary control algorithm was established for form a generic framework for incorporation into other ESS. The binary output can be used for automatic shutdown and/or fire extinguisher control signals and may be also used for maintenance warnings.

These combined benefits provided by off gas monitoring create an opportunity for enhanced control and potentially reduced cost. Early warning provides a means to potentially extend the operational limits of the battery, thus enabling monetization of high value but otherwise "abusive" services, such as occasional high power discharges or low depths of discharge. In addition, the potential for life extension beyond the industry-standard 80% capacity is possible, thus extending system life and revenue. In addition, pathways to reduce redundancy in other sensors (such as voltage and temperature) are possible which may reduce the overall system cost.

Overall, the sensor can be integrated into the BMS or independent of the BMS, or a combination of control methodologies can be created to add redundancy. This is shown in Figure 19.

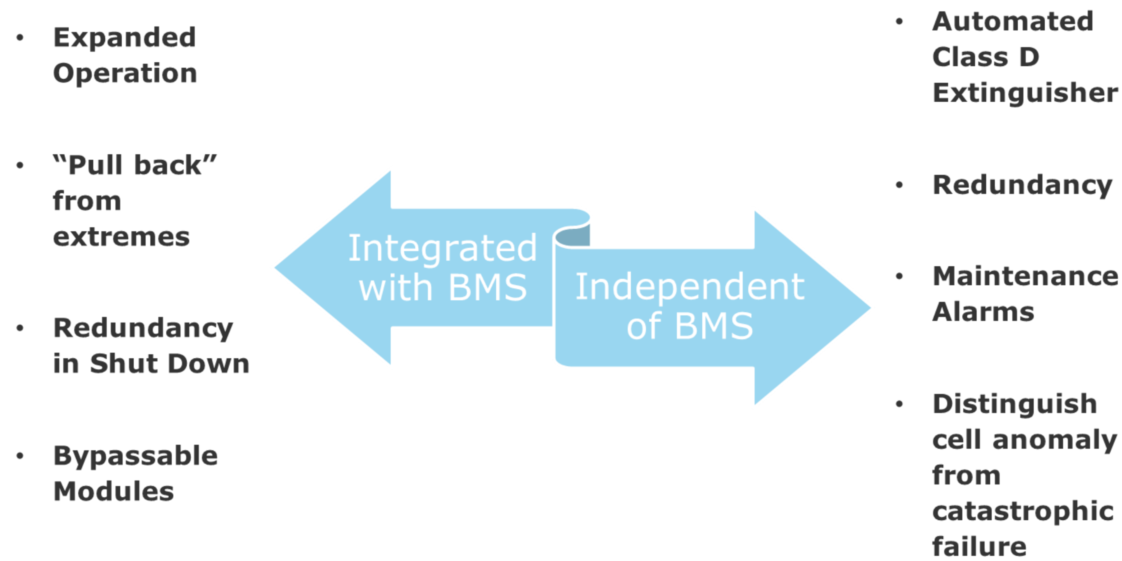


FIGURE 19 **SUMMARY OF POTENTIAL ESS CONTROL BENEFITS.**

APPENDIX: PROGRAM STATISTICS

Total tally: 98 cells tested (not accounting multiple tests on some cells, initial qualification, cycling, and capacity tests)

'Offgassing' is defined as an event which caused the sensor to indicate a response with a sample taken that confirm gas content through Gas Chromatography.

- Cylindrical
  - Overcharge then heat – all 4.4Ah semicylindrical (5 cells tested total)
    - 40% no offgas no failure
    - 20% thermal runaway with offgas warning
    - 20% violent, sudden failure (explosion)
    - 20% offgas but no thermal runaway
  - Heat then overcharge at temp – 4.4 Ah semicylindrical, two additional 18650 cylindrical types (24 cells total)
    - 100% current interrupt device prevented failure
- Pouch
  - Overcharge then heat 40 Ah pouch (10 cells total)
    - 40% offgas but no thermal runaway (one recovered and cycled)
    - 20% offgas and thermal runaway
    - 40% no offgas no thermal runaway
    - 100% of tests at 2x voltage OC (with heat) offgassed and went into thermal runaway
    - Other tests conducted at 4.6 overvoltage, 33% offgassed without going into thermal runaway. Rest did not offgas nor go into thermal runaway
  - Heat then overcharge, 40 Ah pouch (16 cells tested total)
    - 94% offgas and thermal runaway
    - Only dissenting event was a cell that offgassed before voltage was applied, so did not enter into thermal runaway.

Cycling (real world conditions)

- Cylindrical
  - 24 cells tested, 5 offgassing events – 20.3%
  - Tests conducted at max current and 40C ambient temp (14 cells, 2 at high voltage - HAS) or at 0.2V overcharge on each cycle and max charge current (10 cells).
  - 14% of cells under high current and temp offgassed
  - 20% of cells overcharging offgassed
  - No cells went into thermal runaway as the result of these conditions
  - Several cells run at single digit ambient temperatures
- Pouch
  - 14 cells tested: 6 under overcharge cycle, 8 at max rated current and max ambient temp (majority also under voltage abuse conditions)
  - No offgas, no thermal runaway
  - Several cells also run under single digit ambient temperatures

Nail penetration tests – offgas indicated 0.1s after voltage

Cycling cells with intentionally compromised packaging 3 tests (prismatic cells) – 2 tests indicated offgas (on sensor) but GC showed only concentration of unknown alcohols