UNDERSTANDING DOWNSTREAM RISK FROM LITHIUM-ION BATTERY THERMAL RUNAWAY & DESIGNING FOR SAFETY

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Abstract
With continued advances in battery technologies, batteries have become one of the leading solutions for not only portable power applications but also energy storage applications. Because of the high energy density in advanced batteries, one key safety goal is preventing the unintended release of stored energy. A catastrophic failure of a battery pack can occur if one or more cells in the battery pack undergo a thermal runaway event that results in a rapid release of the stored energy in the battery. Thermal runaway can lead to a release of flammable gases and heat, which can potentially result in fire and explosions. The design of effective thermal management systems or fire mitigation systems requires proper quantification of the thermal failure characteristics. This presentation will detail several research activities that have been developed to analyze and quantify thermal safety aspects of batteries, as well as to identify/quantify potential toxicology hazards. This process involves real-time gas analysis from lithium-ion battery failure events, as well as post-failure composition analysis and identification of gas combustion properties. The implications of this work toward designing for safety and integration into risk analyses will be discussed.

Introduction: Thermal Runaway, Risk Analysis, and Design Considerations
Thermal runaway occurs when the temperature of a cell increases in an uncontrolled manner, leading to its failure. This temperature increase generates gases that vent when the pressure inside the cell rises above a design value. For lithium-ion cells, these vented gases are hot and combustible, which may present hazards that require consideration during the design phase of the pack and/or the end-use product. Addressing these hazards thus requires assessing risks associated with battery venting at the earliest stages of the life cycle of a lithium-ion battery system.

For example, the design of large, multi-cell battery packs and systems requires the consideration of cell-to-cell failure propagation. Exponent's experience in battery failure analysis has found that the secondary effects of cell failure, including vent gas combustion, have typically not been addressed in the battery safety standards or guidance until recently. A report entitled "Considerations for ESS Fire Safety" was published in January 2017 regarding work performed by DNV GL for Consolidated Edison in which batteries intended for use in energy storage systems were characterized in order "inform codes writing procedures and first responder training."[2]

The design considerations for the implementation of battery pack systems in specific products will also typically not be addressed by battery manufacturers. Because of the unique use conditions employed by a given battery-powered product, the safety aspects of the battery pack become inherently intertwined with the product itself. For example, a certain electrical device may use a battery pack that is confined in a rigid casing with poor heat transfer characteristics. Poor heat transfer out of the pack may increase the likelihood of inducing thermal runaway, and the rigid casing may increase the severity of a thermal event by confining the energy of single cell failure and potentially inducing other cells into thermal runaway as well. Additionally, different products may be more or less likely to be in close proximity to humans at any given time.

Due to the product specific nature of battery related safety characteristics, manufacturers that employ battery packs in their products have a need to understand how to improve the safety of their devices in the event of thermal runaway. Proper quantification of the hazards posed by battery failures is the first step in obtaining that understanding. Once a manufacturer understands the degree to which battery failure can impact the safety of their products, the manufacturer can integrate the knowledge into design changes before the product hits the market. In some cases, these same analysis are helpful in modifying the design of existing products after field failures show that a safety hazard is present. The work described in the following sections addresses some methods that may be used by battery manufacturers and product manufacturers in assessing the risk of thermal runaway.

The following paragraphs describe the different steps involved in a thermal runaway and summarize the latest quantitative data related to thermal runaway in lithium-ion cells. Results from recent work on small format lithium-ion pouch cells (2.1 Ah, 7.7 Wh nominal) are summarized below. However, the testing and analytical methods used in these studies can be applied to large format cells. The cells consisted of a negative electrode with graphite active material and a positive electrode with $LiCoO_2$ active material. Note that cell chemistry, cell geometry, as well as the way the thermal runaway process is initiated influence the quantitative behavior of the failure.

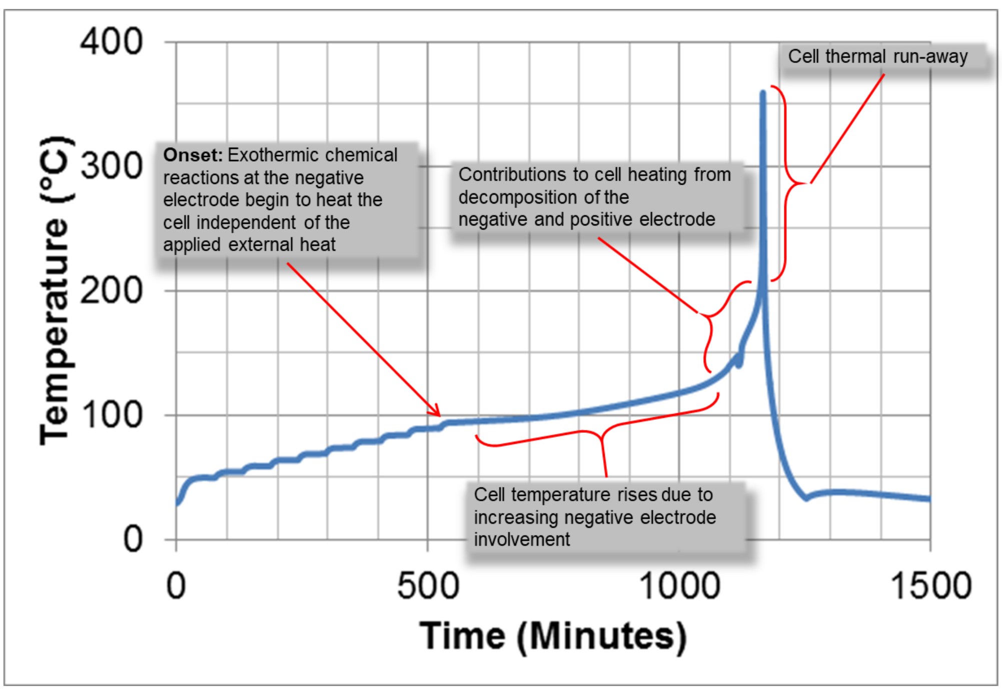

Figure 1. Accelerating Rate Calorimetry data (blue curve) from a lithium-ion cell exhibiting various stages of thermal (in)stability after onset.

All thermal runaway events are a result of a rise in cell temperature. This temperature rise can have multiple causes, including, but not limited to:

- The use of cells in high temperature environments.
- A defect inside the cell can resulting in an internal short circuit, which causes the cell to heat up at the location of the defect.
- Charging or discharging at rates beyond the capability of the cell. Cell internal resistance leads to ohmic heating.
- Electrical contacts external to the cell. For example, both an external short-circuit and/or a loose connection can lead to heat generation.

Consequences of Cell Thermal Runaway and Attempts at Quantification

Cell thermal runaway events typically result in the release of a number of primary thermal effects such as the high temperatures of the cell can and the ejecta (hot gases, molten aluminum, etc.). In a multi-cell battery pack, it is important to understand the temperatures/severity of such events in order to attempt to prevent propagation (i.e. the induction of thermal runaway in additional cells as an effect of the original failure). There are a variety of materials and/or design methods toward this goal, which are not the focus of this work.

Secondary effects of thermal runaway can include ignition of potentially combustible/explosible gas that is emitted from the cell(s). This gas can fill any void space in the battery pack and larger device and, if ignited, is potentially more catastrophic than primary effects (e.g. explosion). In contrast to cell-level safety devices (e.g. cell vents, PTC) and strategies, this vented gas is not mitigated by cell-level safety components.

With the goals of characterizing and quantifying the failure scenarios from thermal runaway and secondary effects, some calorimetry methods can be used to determine self-heating rates and onsets, as well as combustion rates. These calorimetry methods include Accelerating Rate Calorimetry (ARC; example in Figure 1) and Oxygen Consumption Calorimetry (i.e. Cone Calorimetry). For example, below in Figure 2 is an example of Cone Calorimetry data from measurements conducted on ~2 Ah lithium-ion cells.

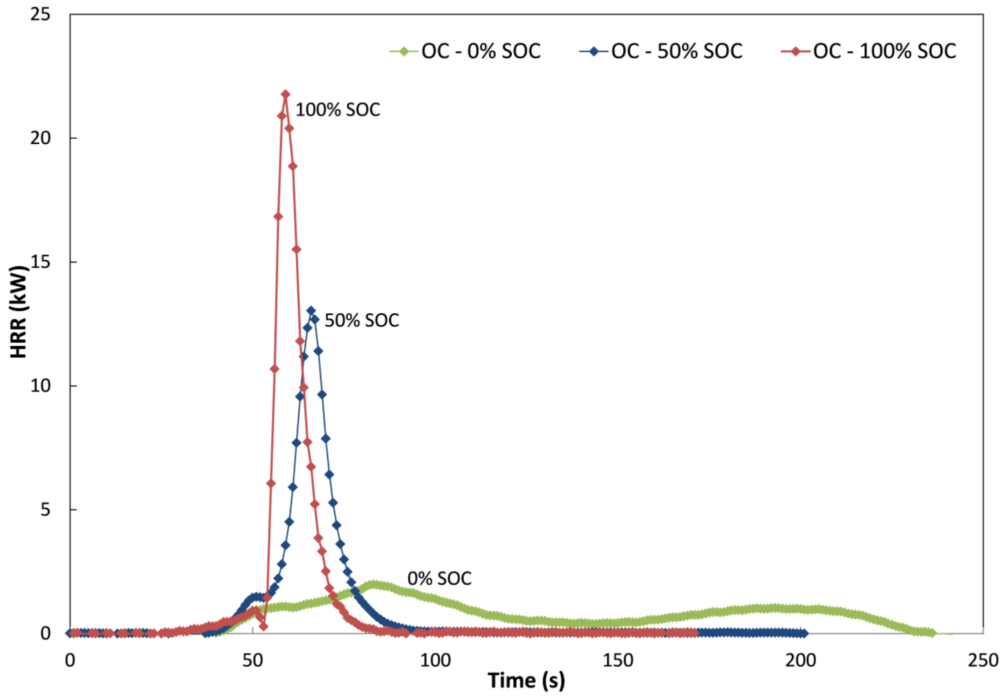

Figure 2. Heat release rate from thermal failure of ~2 Ah lithium-ion cells at 3 states-of-charge, measured via Cone Calorimetry.

These methods tend to focus on the primary consequence of cell failure and generally do not characterize fully the secondary effects of the potentially combustible vented gas. In order to characterize these secondary effects, the vent gas needs to be collected and quantified in terms of both volume and composition. The gas mixture should then be tested for combustion properties.

Battery Vent Gas Collection and Analysis

Exponent has designed and built sealed chambers of various sizes which allow control, collection and containment of gases vented from battery failure and other scenarios. The largest of which being a ~60 L sealed pressure vessel that has accommodated failures of lithium-ion cells up to 200 Ah in capacity (Figure 2). The contained vent gases are collected from the chamber into either gas-tight syringes or summa canisters before submission for analytical gas composition analysis. In addition to the composition of the gas, the rate and amount of gas generated at STP can be calculated using internal pressure and temperature measurements of the chamber.

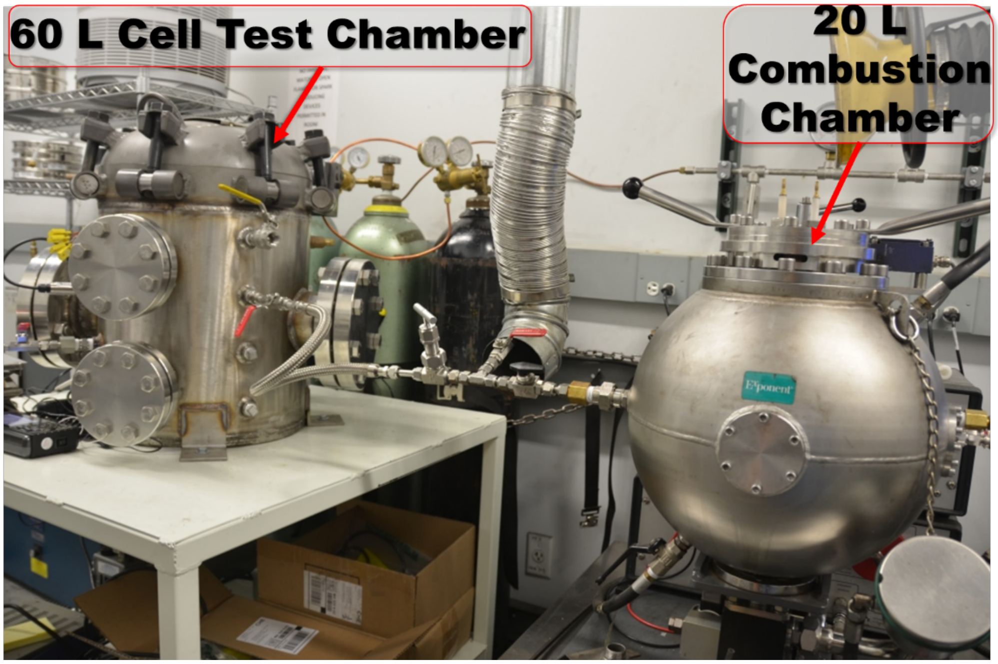

Figure 3. Photo of a battery vent gas collection chambers mated to a combustion chamber.

Exponent has performed composition analysis of the vented gases at various states-of-charge by heating the cells until thermal runaway failure. The results (Figure 4) show that the composition varies with state of charge, and notably contains a significant portion of hydrogen. Comparisons were made to past literature for gas composition from failed lithium-ion cells, though the portion of hydrogen was significantly higher 5x-6x higher by volume. It is notable that the prior work involved gas collected from ARC testing over longer-time scale cell failures.

Figure 4. Li-ion battery vent gas composition at various SOC's via gas chromatography. The amount of total gas generated was 0.8 L, 2.5 L and 6.0 L at 50%, 100% and 150% SOC (~2 Ah cell), respectively.

Gas	50% SOC (%vol)	100% SOC (%vol)	150% SOC (%vol)	Roth et al.[1] (%vol) Test 1/Test 2
Carbon Dioxide	32	30	20.9	61.4 / 75.8
Carbon Monoxide	3.61	22.9	24.5	15.1 / 6.4
Hydrogen	30	27.7	29.7	5.1 / 5.9
Total Hydrocarbons	34	19.3	24	7.4 / 1.9

In gases vented from cells failed using the same external heating method, the combustion properties were tested using spark ignition in the combustion sphere in Figure 3. The ratio of battery vent gas to atmosphere was metered to adjust the fuel/air ratios to allow for determination of the P_{max} (maximum pressure difference) and dp/dt (rate of pressure rise) for the resulting explosion. When these two values approach zero, the lower and upper explosion limits (LEL and UEL) can be identified. This effectively describes a fuel:air ratio that is either too 'lean' or too 'rich' for combustion/explosion. These results are presented in Figure 5 both in terms of P_{max} (P_m) and dP/dt, along with comparison to the combustion properties of methane and hydrogen.

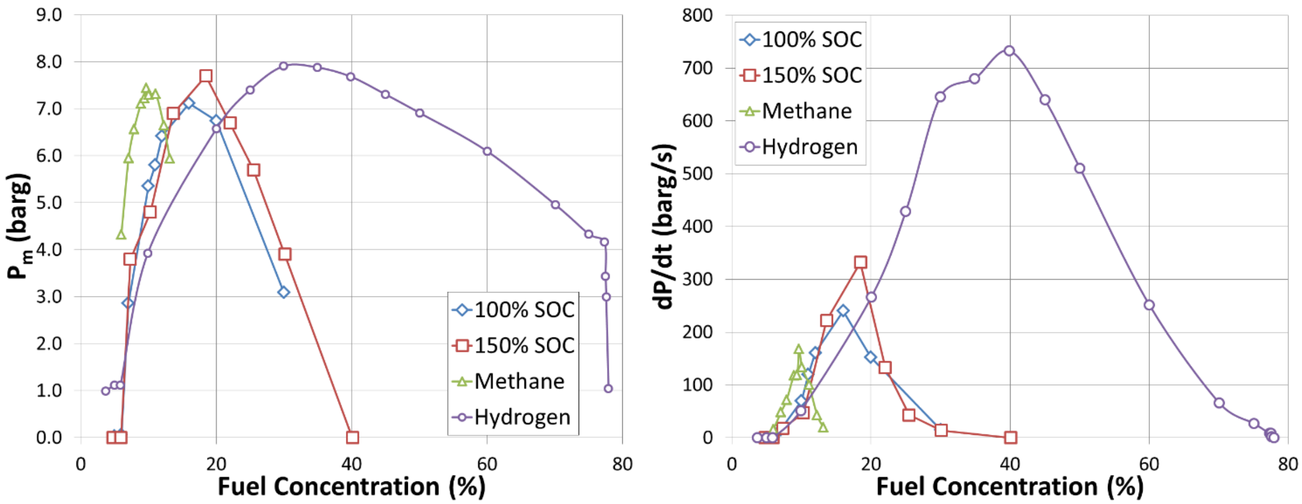

Figure 5. Maximum pressure rise (Pm) and pressure rise rate (dP/dt) as a function of cell vent gas : air for a thermally-failed ~2 Ah lithium-ion pouch cell. Each point (i.e. square, circle) represents a single.

The notable feature of the battery vent gas characteristic(s) is that the fuel concentration range of explosibility is much wider than methane, though not at as wide hydrogen. It is proposed that this characteristic is due to the large hydrogen component in the vent gas, as was measured via GC (Figure 4).

Summary

Thermal runaway of batteries such as lithium-ion chemistry exhibit both primary and secondary effects in their failure. With the secondary effects generating many liters (per cell) of potentially explosible gas that can fill a battery, device or enclosure, they may be more catastrophic than the primary effects. Gas vented from lithium-ion cells contains a significant portion of hydrogen, which leads to a wide explosibility range that should be considered when designing a battery pack and application.

References

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BATTERY SYSTEMS IN A SUBSTATION: MANITOBA HYDRO'S EXPERIENCE WITH ALTERNATIVE TECHNOLOGIES

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Introduction

Utilities use stationary battery systems in substations for such purposes as stand-by power supply or as a power source for communication systems. With stringent limitations on space and increasing requirements for safety and reliability, utilities need to consider new battery chemistries to enable reliable, secure, space-effective, and cost-effective substation energy storage. Despite their higher initial costs, Manitoba Hydro recently began investigating the possibility of employing alternative, high-energy battery technologies for use in specialized applications where otherwise high installation costs would most likely make conventional VLA technologies less competitive. Two examples include using these new technologies in isolated communities, where operations are hampered by high installation, transportation, and maintenance costs and when their small footprints obviate the need to install expensive additional structures such as "Ready-to-Move" (RTM) trailers in particularly cramped substations. Such potential benefits prompted Manitoba Hydro in late 2016 to fund a two-year project investigating the suitability of both Sodium Nickel Chloride and Lithium-Ion batteries, their chargers, and their battery management systems (BMSs) for specific substation standby applications. The purpose of this project was to generate reliable characteristics of the aging process of Lithium-Ion and Sodium Nickel batteries for substation applications by recording and analyzing battery performance in their native substation applications and to determine whether they can be considered viable alternatives to conventional battery technologies. Manitoba Hydro purchased and tested a Lithium-Ion battery system from Saft and a Sodium-Nickel battery system from FIAMM for evaluation purposes.

Although this project is expected to be completed on time, numerous practical issues have emerged to delay the completion of many experiments. This paper will present some of these issues and provide initial data generated while evaluating these new technologies' performance under "real-world" conditions.

Existing sizing procedures

While there is continuous work towards their development, IEEE has not yet published technical guidelines that outline sizing standards for either lithium-ion or sodium-nickel battery systems. In the absence of such technical standards, the batteries for this project were sized using lead-acid technologies and NERC guidelines as a reference point. Although further evaluation will likely determine that new battery technologies require different sizing methodologies than conventional chemistries, they provide a good starting point and enough information for experimentation i.e. Capacity requirements, Current magnitude needs.

The duty Cycle used in Manitoba Hydro's stations is shown on figure 1. Current Magnitudes and the total duration of each section is determined, based on following factors [5]:

- All steady State DC loads
- The worst-case protection events
- The DC loading for each switching device in the station
- Number of switching devices in the station

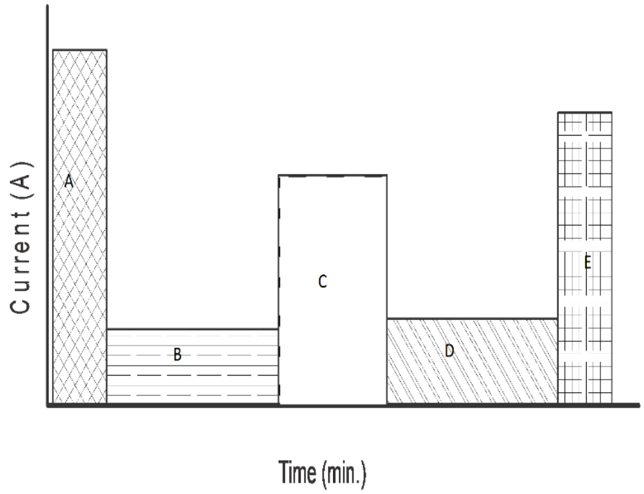

Figure 1. Typical duty cycle station load profile

Table 1. Duty Cycle example		
Section on Figure 1	66kV station	138kV station
A	266A -> 1 min	67A -> 1 min
B	8.1A->239 min	16A ->239 min
C	120A -> 5 min	30A -> 12 min
D	8.1A->234 min	16A ->227 min
E	128.1A->1 min	46A ->1 min

Lithium Ion Installations

The first installation was commissioned in the summer of 2016 at a Manitoba Hydro training center. The location was chosen as it would allow frequent cycling and usage of the batteries in their intended application. The Li-ion system (Figure 2) consisted of three parallel strings each having a 90 Ah capacity. There were five 24 V modules (Figure 3) in series in each string. This installation was suitable for a substation requiring 180 Ah and one string serving as redundancy. The initial float voltage was set to 125V since that is the most common voltage used in substations and it also corresponded to about 80% SOC (State of Charge). The float voltage later changed to 140 V to correspond with 100% SOC.


Figure 2. Li- ion installation


Figure 3. 140 V string

In December of 2017 two additional Li-ion systems were commissioned for experimentation and testing purposes. Four strings of three 24 V modules were each mounted on a rack and placed inside an oven (Figure 4, 5). The strings battery management systems were placed outside the oven to protect the electronics, and to allow for easy connection of the diagnostic tools (Figure 5, 6).It is important to note that cell management is done by electronics inside each individual module and therefore are subjected to increased temperature of the oven. It is expected that exposing the batteries to oven temperatures would accelerate the battery aging process [1]. The oven was set at 60°C which is the maximum temperature recommended by the manufacturer. Each string was stored on a different SOC. Module 1 at 20%, Module 2 at 50%, Module 3 at 80%, Module 4 at 100% and connected to the charger.

Figure 4. String inside oven

Figure 5. Oven-charger-BMS setup

Figure 6. BMS

Lithium Ion Testing

The Battery Management Module (BMM) of the batteries allowed a PC connection and use of diagnostic software to record various battery parameters (e.g. Minimum/Maximum Cell voltage).

As an initial test the values for the instantaneous resistance were calculated after performing a Current-Off Test [2], using the current discharge profile shown on Figure 7 . Although the method is not the most accurate it was chosen for its simplicity and can provide a comparison tool.

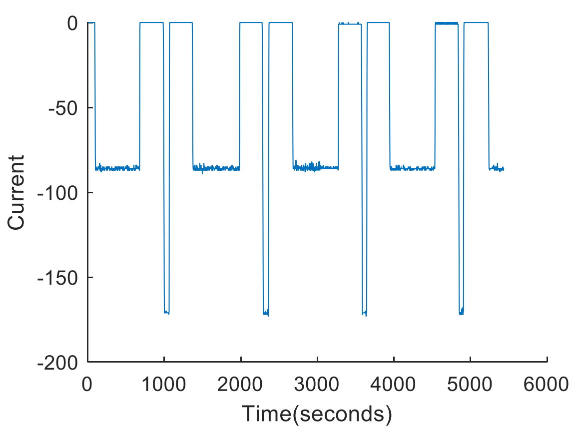

Figure 7. Discharge profile 140V system

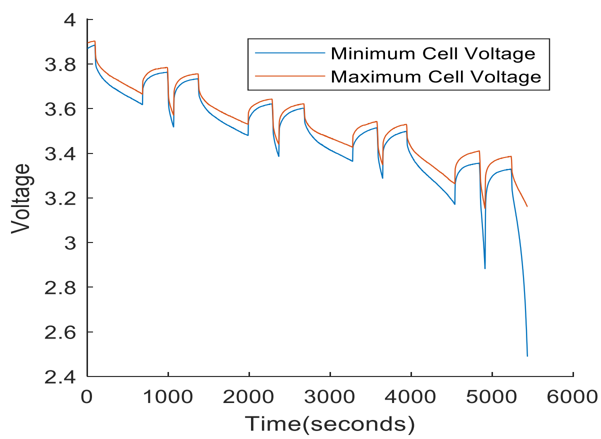

Figure 8. Cell Voltage 15month old batteries

The batteries installed in the Training Centre were periodically completely, 100% depth of discharge (DOD), discharged at 1C (1-2 times a month), and were often used to power a circuit breaker, motor operated disconnects, relays and re-closers. Table 2 shows a comparison between the instantaneous internal resistances after roughly 15 months of usage.

Table2.InstantaneousResistance calculated 15 months apart.		
Depth of Discharge (DOD)	New Batteries R(mOhm)	15month batteries R (mOhm)
27%	0.68	0.9
31%	0.62	0.76
49%	0.53	0.75
53%	0.64	0.86
69%	0.36	0.75
73%	0.54	0.85
89%	0.76	1.929
93%	0.86	N/A

Even when factoring in calculation errors from the methodology, and test procedure variations there is a noticeable increase in internal resistance after 15 months. and particularly on higher DOD. The 15-month batteries were unable to complete the intense discharge profile of Figure 7. Internal resistance monitoring will continue to determine the correlation between time used and internal resistance. Eventually we hope to have enough data to develop a model based on Randles circuit [4] to predict and assess batteries performance. It is important to note that batteries installed in the field will be discharged far less often if at all hence the increase of the internal resistance is expected to be a lot lower.

A similar procedure was used for the batteries stored at 60°C. The current off method was again used for the determination of the internal resistance. A different discharge profile (Figure 9) was used, however, and it was tailored to the reduced voltage of a 3-module system (83V).

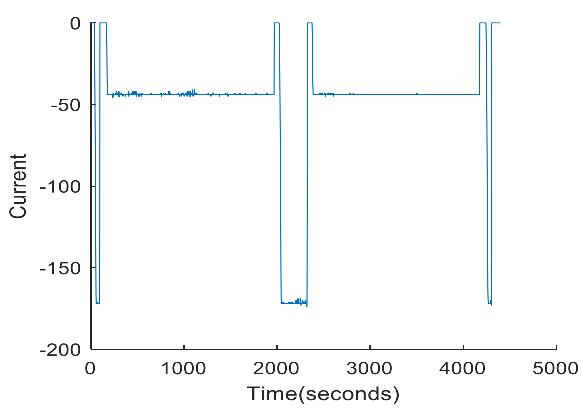

Figure 9. Discharge profile for 83V system

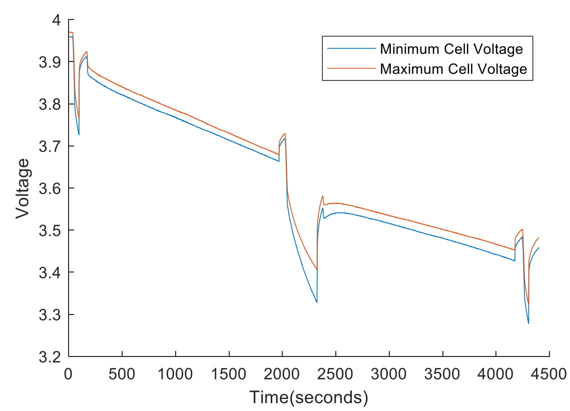

Figure 10. Cell Voltage 83V system new Batteries

Table 3 shows the measured internal resistances of the batteries after being stored at 60°C for two months. The initial results have shown that batteries stored on lower % SOC have a lower internal resistance. Further measurement will be taken to determine if the trend continues although results seem to agree to those obtained by [3].

Table 3. Batteries stored at 60°Celsius				
DOD	OVEN 20% SOC R(mOhm)	OVEN 50% SOC R(mOhm)	OVEN 80% SOC R(mOhm)	OVEN 100% SOC R(mOhm)
2%	0.46	0.49	0.68	0.6
30%	0.48	0.69	N/A	0.71
40%	0.63	0.67	0.72	0.65
54%	0.44	0.47	0.67	0.69
59%	0.47	0.51	0.66	0.64

Although performing pulse tests and measuring internal resistances is expected to be of future use in statistical modeling what is also of interest in how batteries perform on a duty cycle following the pattern discussed in the sizing section. Due to time constrains an accelerated and more intense duty cycle was used (Figure 11), over the one normally used in the field.

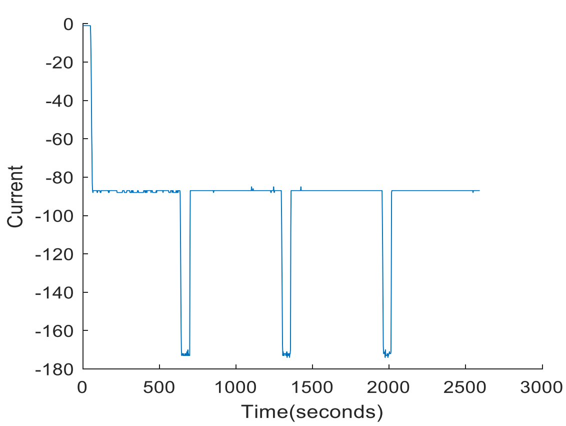

Figure 11. Intense Discharge Current profile.

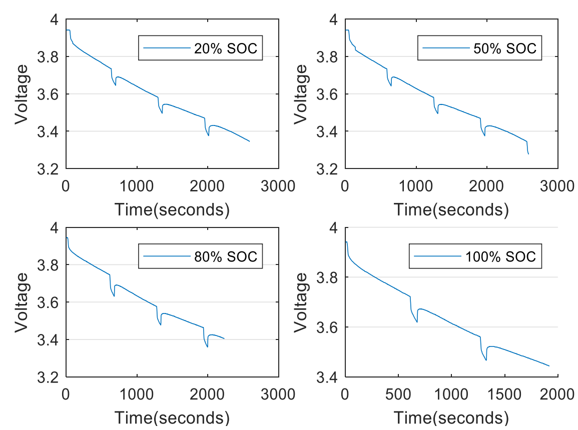

Figure 12. Minimum Cell voltage for batteries stored at 60°C

As it is expected from the internal resistance discrepancies, the systems performed a lot differently and there are clear differences in the discharge ability of each string (Figure 12). The systems stored at lower SOC (20% and 50%) were able to discharge 67 Ah and 69 Ah before critical voltage. On the other hand the systems stored at 80% and 100 % were only able to discharge 56Ah and 48 Ah. Further tests are required to find the cause of these differences as they are greater than expected. The temperature of the modules was monitored with both the BMS diagnostic software and FLIR infrared camera and there were no large deviations in temperature between modules<2°C.

To further test the difference, the strings stored at 50% and 80% SOC were discharged with 1C from 100% SOC (Figure 13). The discharged capacity was measured as 75Ah and 63 Ah before the critical voltage was reached which is a significant decrease from the rated capacity.

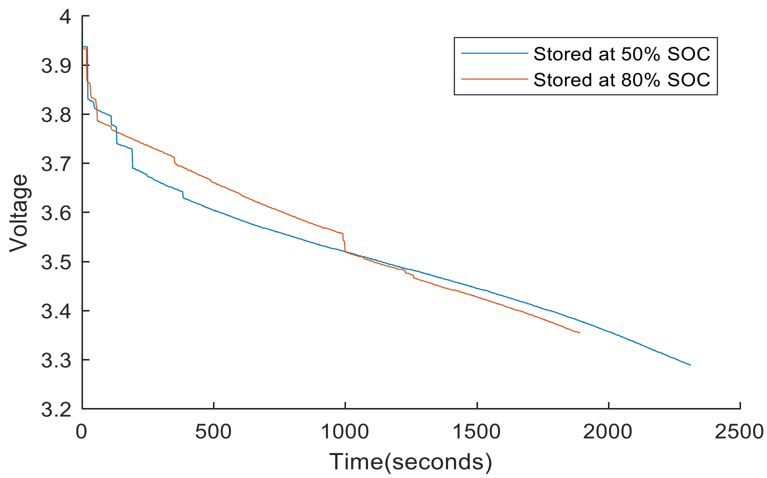

Figure 13. – 1C discharge from batteries stored at 60°C

Sodium-Nickel

The second Chemistry was a Sodium Nickel Chloride battery from FIAMM (Figure 14). The system consists of two modules rated at 110 V with an 80 Ah capacity. Their float voltage was set at 130 V with rest voltage being at 117 V. This was lower than the desired but at the time of purchase there was no option available for the desired substation voltage.

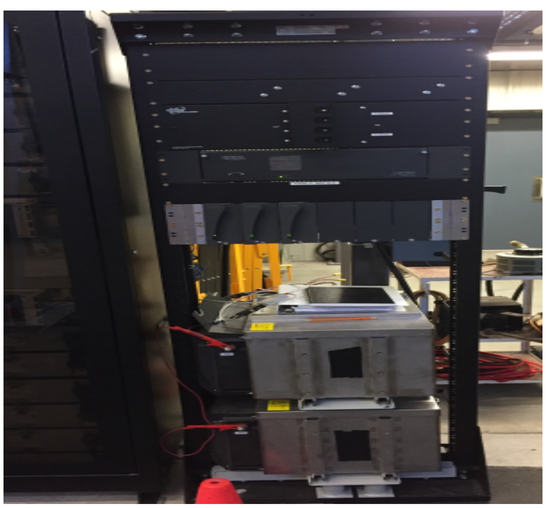

Figure 14. Sodium-Nickel installation

Figure 15. Switch between sodium nickel and li-ion.

Our testing currents were limited to 125 A because of the system internal circuit breaker. The biggest concern with Sodium-Nickel was whether a high current would cause the internal temperature to reach critical values and thus shut down the battery. With our test that was achieved using a current of 110 A for <30 min. Two different load profiles were tested.

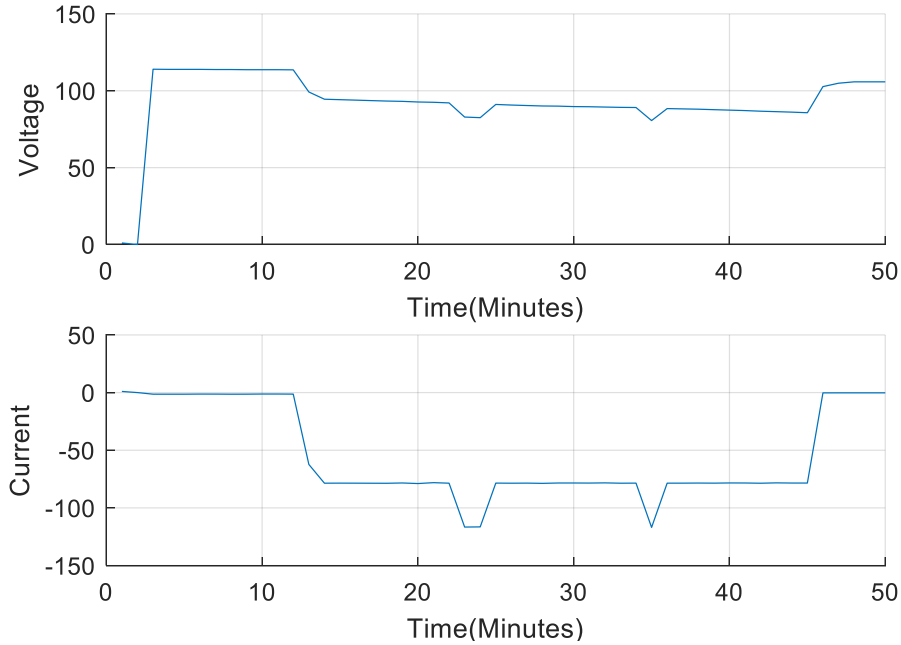

Figure 16. Voltage (Top) and Current Discharge Profile (Bottom)

In this case the voltage dropped from 114 V to 79.6 at the end of the Test after discharging a capacity of 45 Ah.

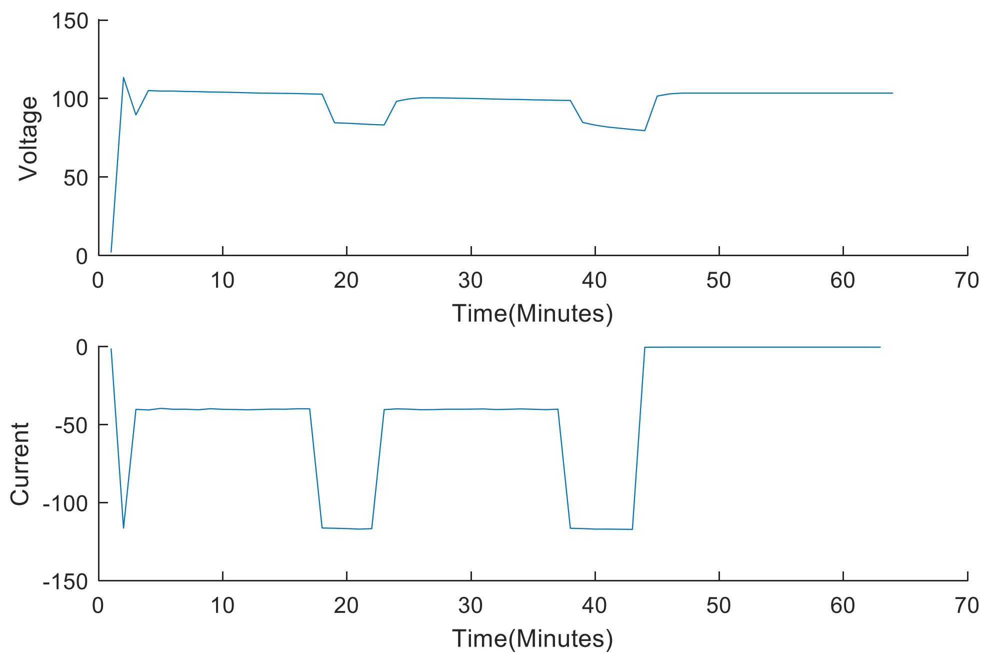

Figure 17. Voltage (Top) and Current Discharge Profile (Bottom)

In this case the voltage dropped from 114V to 85.7 at the end of the Test discharging 43.5Ah.

In both cases the BMM terminated the test. The internal temperatures of 340°C were very close to the disconnect point of 350°C. We are still investigating ways to artificially age the modules and for the time being we are familiarizing with the technology and record data. No significant changes in performance were observed over 15 months, but arguably those batteries were tested less that the lithium-ion but at the same time was the battery of choice of the training crew.

At the training facility the staff tried a close operation on a breaker and the breaker failed to close because the battery was not in the circuit. The technician did not realize that the battery had tripped because there was no indication on the charger or battery. This caused the close coil to not operate and burnt the windings of the coil.

Two more sodium nickel systems are expected to arrive in March of 2018 for testing purposes.

Observations

The needs of a utility when choosing battery banks can be summarized as follows:

- Amp hour sizing
- Physical size (footprint)
- Right voltage
- Life duration guarantees
- Compatibility with different chargers
- Simplicity
- Cost
- Maintenance intervals and procedures

Both technologies are fairly new to the substation bank market and were also new to us thus setbacks, especially under test conditions, were expected. We would like to share some of the difficulties experienced both from testing/planning side as well as a field side. None of the difficulties are insurmountable and are presented to serve as a checklist for other utilities before installing similar technologies.

Lithium-ion

- Difficulties in connecting to diagnostic and recording results
- Unable to connect to individual strings must go through Master Battery Management Module (MBMM)
- In the four string system there is significant back charging between strings, with charging currents in excess of 70A for an individual string.. We are not aware if this is a desired behavior and if it is, why is charging limited to 40 A to protect the system.
- Limited to using a specific charger, fear of future compatibility issues
- No Sizing standards
- Random tripping of strings at the training center location. No testing was being done at the time and when staff would check on the charger an alarm was up indicating a string had tripped. We have yet to determine the cause.

Sodium-Nickel

- Recording intervals high in diagnostic software.
- Difficulties in disconnecting and connecting the two strings
- Less literature available for aging, harder to model behavior and evaluate battery life
- Capacity is affected by discharge current and can make sizing difficult. Maximum capacity is available at C/4
- No Sizing standards

- The battery voltage is only 110 Vdc whereas the station voltage preference is between 125-135 Vdc

Field Experiences
Lithium-ion

- Issues and difficulties with the way alarms are set
- Seems complicated
- Expensive, current system use components that can add significant cost and are unnecessary (e.g. a 200 A circuit breaker)
- Have to bypass the BMS to charge a cell if voltage drops low enough

Sodium-Nickel

- Issues with alarms, although FIAMM did have a solution to bring out an external alarm to wire into a charger digital input. This was tested but the alarm does not appear to work. Currently working with supplier on a solution.
- Charge current limited to 14A. This makes it difficult to achieve the required recharge time of 8-12 hours after a complete discharge.
- There is no need to store batteries under a float charge. Shelf life of stored replacement batteries is not a concern.
- Little to no concern for ambient temperature at the site. Batteries are not affected by high or low operating temperature.

In closing

The market will need batteries with higher power density and both li-ion and sodium-nickel-chloride will be contenders. Both technologies satisfactorily meet substation needs. Further tests are needed to evaluate their long term performance and sizing standards will need to be determined and later published. Our plan is to build a test schedule for the sodium nickel system, to continue li-ion testing and to work on the maintenance standards needed for both technologies. If deemed practical, Manitoba Hydro intended to generate purchase specifications and maintenance criteria for caring for these batteries during their operational lifetimes. Initial failure modes, components, and subcomponents for these apparatus along with Mode/Cause/Task (MCT) analyses and P-F curves are to be developed in order to establish the most effective maintenance tasks and intervals with respect to both system reliability and lifecycle costs. These reliability and lifecycle costs would then be compared to those of vented lead-acid (VLA), valve-regulated lead acid (VRLA), and Nickel-Cadmium ("Ni-Cad") battery technologies. Additionally, specific input parameters and weightings will be required in order to develop Asset Condition Assessment/degradation and Asset Health Indices, which the utility industry is increasingly developing for each of their apparatus in order to establish systematic repair/replace criteria that can be demonstrated to regulatory bodies. As a final point because these battery technologies are intended to be used in an electric utility setting, a set of purchase specifications, tender evaluation matrices, commissioning and maintenance documents will also be required.

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