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III.B Battery Testing

III.B.3 Battery Safety Testing

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Project Introduction

Abuse tests are designed to determine the safe operating limits of HEV\PHEV energy storage devices. Testing is intended to achieve certain worst-case scenarios to yield quantitative data on cell\module\pack response, allowing for failure mode determination and guiding developers toward improved materials and designs. Standard abuse tests with defined start and end conditions are performed on all devices to provide comparison between technologies. New tests and protocols are developed and evaluated to more closely simulate real-world failure conditions.

While robust mechanical models for vehicles and vehicle components exist, there is a gap for mechanical modeling of EV batteries. The challenge with developing a mechanical model for a battery is the heterogeneous nature of the materials and components (polymers, metals, metal oxides, liquids). Our work will provide empirical data on the mechanical behavior of batteries under compressive load to understand how a battery may behave in a vehicle crash scenario. This work is performed in collaboration with the U.S. Council for Automotive Research (USCAR) and Computer Aided Engineering of Batteries (CAEBAT). These programs have supported the design and development of a drop tower testing apparatus to close the gap between cell/string level testing and full scale crash testing with true dynamic rate effects.

This work is discussed in further detail in the CAEBAT annual report section. Additional modeling efforts lie in being able to better predict failure propagation within larger battery systems. Sandia's battery safety testing provides testing support to better aid in thermoelectrical model development at NREL and SNL.

Materials characterization to better understand batteries that have undergone abusive conditions is of interest. Our partnerships with Argonne National Lab (ANL) and Oakridge National Lab (ORNL) through the Post Test Analysis Program for ABR, spans the building of cells with known materials (ORNL), overcharge testing to various states (SNL), and the posttest analysis of the cells (ANL). In addition, testing to support the Si-Deep Dive Program has been leveraged to gain a better understanding of the safety implications for these materials.

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Calorimetry testing has historically been performed on 18650 cells of ~1.5 AH or lower. Testing has been performed to understand how best to apply data from this testing to larger scale formats and cells of increasing energy density. This will inform future work performing ARC testing of new high energy chemistries and how those results might apply to larger format cells.

The ability to fast charge electric vehicles addresses two major points of consumer EV adoption: range anxiety and convenience. However, fast charging also introduces new degradation mechanisms in the battery, and may contribute to new failure mechanisms. In fact, adverse effects seen during fast charge resemble battery abuse in several ways. In the cathode, fast charging is known to cause localized heating, which can lead to breakdown of active materials, electrolyte, and binder. It can also cause localized over-delithiation, damaging the cathode structure. In the anode, the primary danger is lithium plating, which occurs if lithium diffusion into the cathode can't keep pace with high rate Li+ delivery to the anode. The anode can also be host to Li+ depletion in the adjacent electrolyte, causing unexpected electrolyte changes and double layer effects. Two common abuse scenarios, overcharge and thermal ramp, result in similar effects. Overcharge is known to cause high voltage breakdown of separator, binder, electrolyte, and cathode material. It also causes over-delithiation in the cathode, as well as lithium plating on the anode. Thermal ramp causes cathode and separator breakdown, SEI layer breakdown, and other electrolyte effects. Because of the shared effects between fast charging and abuse, a project was undertaken to quantify the effects of fast charging on abuse response.

Objectives [Use EERE_Head_03_Shaded]

- Provide independent abuse testing support for DOE and USABC
- Abuse testing of all deliverables in accordance with the USABC testing procedures
- Evaluate the impact of scale of stored energy on the thermal runaway characteristics of lithium ion batteries, with an eye to informing how to interpret accelerating rate calorimetry data of developmental cells.
- Develop initial test methods for evaluating the impact of high rate charging on battery safety performance.
- Provide testing data to support failure propagation model (NREL)
- Provide testing support for ABR Post Test program (INL/ANL)

Accomplishments

- Completed testing of all USABC deliverables to date and reported results to the USABC TAC
- Current abuse testing procedures published as a Sandia report SAND
- Developed method to use a laser to induce a short within cells
- Testing support for CAEBAT activities
- Extended failure propagation modeling efforts with NREL using testing data
- Provided testing support for several cell chemistry types (NMC, LFP, and Si) to varied levels of overcharge in support of the ABR post test program (ORNL, SNL, and ANL)
- Evaluated impact of extended high rate charging on abuse response of pouch format cells

- Impact of cell scale and state of charge on Accelerating Rate Calorimetry results examined

Approach

Abuse tolerance tests evaluate the response to expected abuse conditions. The goals of abuse and safety testing include a) testing to failure of energy storage devices and documentation of conditions that caused failure, b) systematic evaluation of failure modes and abuse conditions using destructive physical analysis (DPA), c) provide quantitative measurements of cell/module response, d) document improvements in abuse response, and e) develop new abuse test procedures that more accurately determine cell performance under most probable abuse conditions. Electrical (overcharge/overvoltage, short circuit, over discharge/voltage reversal, and partial short circuit), mechanical (controlled crush, penetration, blunt rod, drop, water immersion, laser induced short circuit, mechanical shock and vibration) and thermal abuse (thermal stability, simulated fuel fire, elevated temperature storage, rapid charge/discharge, and thermal shock cycling) cover the main categories of possible conditions evaluated. These techniques are applied to USABC deliverables and the results reported to DOE and USABC.

Research and development batteries used for simulating internal short circuits, propagation testing (alternative initiators and passive thermal management), impact of cell scale evaluation, and safety impacts of elevated charging rates are based on commercial-off-the-shelf (COTS) $LiCoO_2$ 18650 and pouch cells, NMC and NCA 18650 and pouch cells, and LFP 18650 (designed for energy) and 26650 (designed for power) cells. Cell failure and thermal runaway initiated by various methods were investigated this FY, including overcharge, laser initiation, and mechanical nail penetration into a single cell within a pack.

Results

The impact of total energy within cells on thermal runaway as well as the scalability of Accelerating Rate Calorimetry (ARC) testing was examined by testing cells of various capacities as well as cells at various states of charge. ARC has been used by Sandia to evaluate the total energy as well as the onset and kinetics of thermal runaway processes, however the bulk of this testing has been done largely on 18650 format cells with less than 1.5 AH of capacity. This work is to better understand how testing of cylindrical format cells can be applied to large format pouch cells, and how the thermal runaway scales as the energy density of a cell increases. This testing was performed on commercial off the shelf (COTS) NMC cells. Summary of these results are shown in Figures 1-2.

Figure 1 shows the results of increasing state of charge within 18650 cells, and in particular shows how lower states of charge impacts thermal runaway. The behavior at 40% SOC shows behavior similar to that seen for higher states of charged, albeit at lower total heating rates. At 20% SOC, an onset similar to that observed for higher states of charge was observed, however the overall kinetics and total energy was significantly reduced, with a relatively low peak heating rates observed. At 0% SOC the exothermic reactions are limited primarily to the effects of electrolyte decomposition as seen in Figure 1 (right). This shows a fairly high onset of any exothermic reactions, as well as relatively limited peak heating rates. Some effects are still observed, however, showing that some exothermic behaviors are still possible even in absence of stored energy.

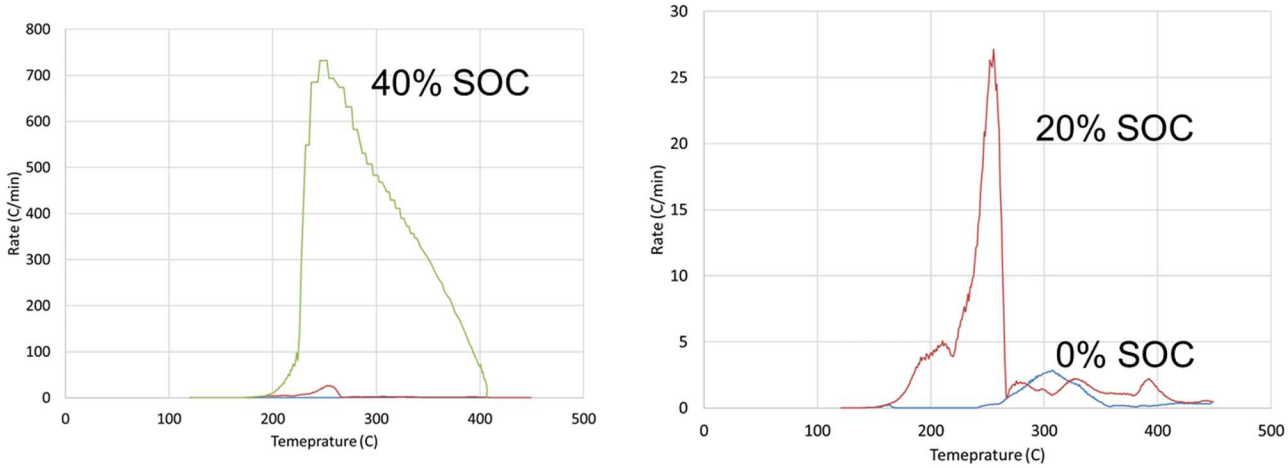

Figure 1

Comparison of cells of varying size is ongoing, with 15 AH and 10 Ah cells shown in Figure 2 below. The kinetics in this case do not show expected patterns with regards to size, with fairly high heating rates observed in both cases. The higher heating rate however was observed in the lower capacity cell, which also had a lower onset of thermal runaway than the larger format cell. This is an early indication that there may be a limit on at least how rapid thermal runaway can occur in large format cells. An evaluation of the total energy of these cells shows a more linear relationship, with the 10 AH cell having a total enthalpy of runaway of ~142 kJ and the 15 AH cell having a total enthalpy of ~189 kJ. While the runaway of the larger cell was at a lower rate, it drove the cell to a significantly higher temperature with the increased energy content.

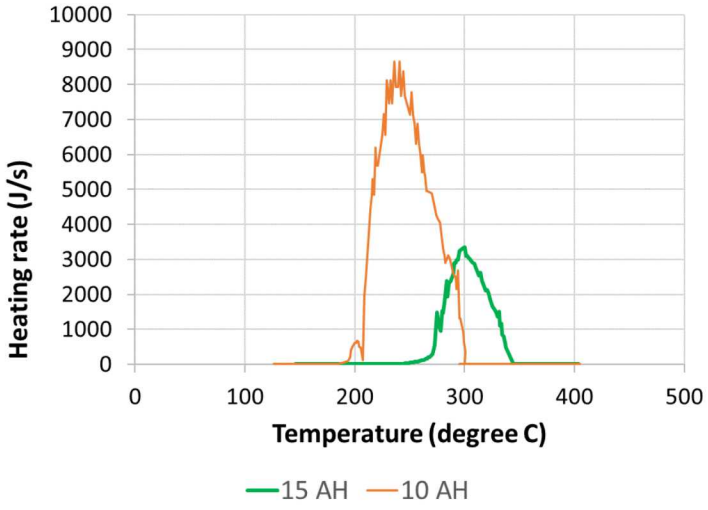

Figure 2

To establish the relationship between fast charge and abuse response, we cycled 10Ah commercial off-the-shelf (COTS) cells up to 300 cycles with charge rates of both maximum specification (1C) and 1.5x maximum specification (1.5C). COTS cells were chosen for ease of procurement and cost constraints. Relevancy to automotive cells was established by observing that COTS cells are typically over-designed, thus adverse effects in COTS cells would only be amplified in automotive cells. 1.5C was chosen as the high charge current

due to limitations in cell rate capability. Abuse response, voltage profile, and dQ/dV were analyzed to look for effects on abuse response and markers of cell damage.

Figure 3 highlights the relationship seen between charge current, cycle number, and overcharge failure SOC. During overcharge tests, it was observed that with increased cycling, cells failed at lower SOCs. Some data suggested earlier failure (thermal runaway) with higher charge rate, but the data was not consistent. It should be noted that even after 300 cycles, runaway SOC was still 175%, well beyond the normal stopping point for cell charging. Runaway temperature during overcharge also decreased as cycles increased.

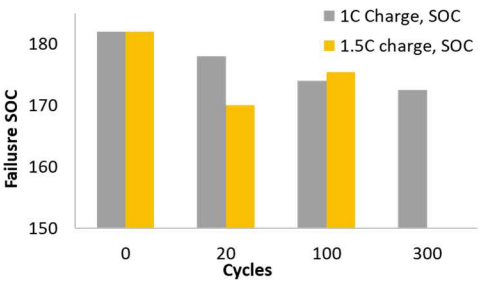

Figure 3: Failure SOC during

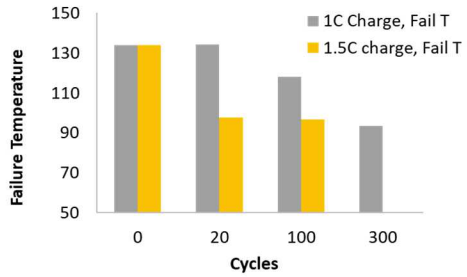

Figure 4: Failure temperature during overcharge

Figure 4 shows the effect of cycles and cycling current on failure temperature during overcharge. Like SOC, failure temperature also decreased with higher cycles. There was also a clearer decrease in failure temperature with higher charge rate. The worst case showed runaway at about 90°C, which was a 30% drop in runaway temperature. This suggests that processes within the cell during fast charge are lowing the resistance of the cell, causing less heat to be generated during otherwise comparable degrees of overcharge.

Figure 5 shows the effect of fast charge cycles on thermal ramp failure temperature. One outlier was observed but otherwise the failure temperature was unchanged. This further confirms that changes in the cell affected cell resistance, but did not introduce chemical changes such that failure occurred at lower temperature during the ramp.

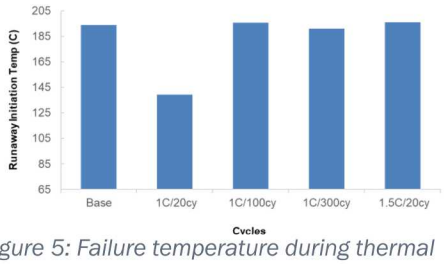

Figure 5: Failure temperature during thermal ramp

dQ/dV analysis (Figure 6) reveals a signature process at about 8% SOC; that peak shows a lower dQ/dV energy flux at later cycles for the fast charged cell compared to the base cell, further indicating a general lowering of resistance in the fast charged cell. Also, the fast charged cell shows a second dQ/dV humpabout 15-20% SOC not seen at all in the standard-charged cell. This could be sign of a key process that changes the fast charged cell's resistance, and consequently its failure behavior.

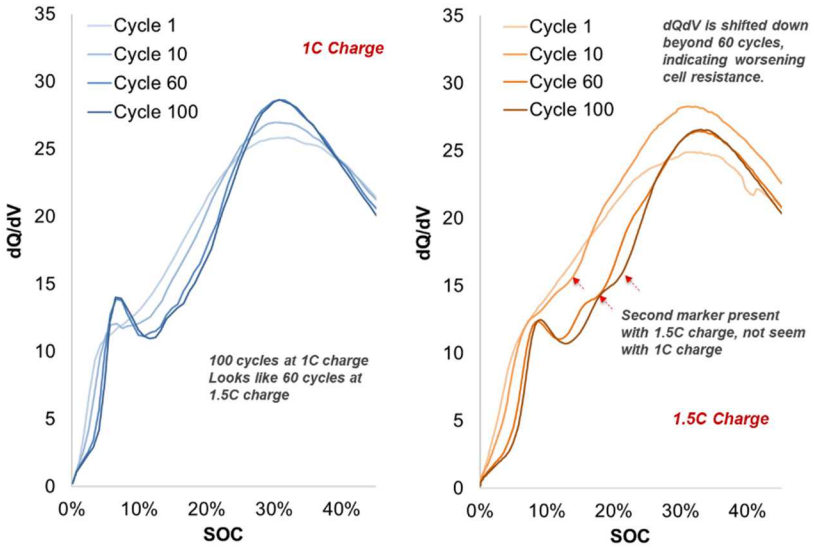

Figure 6: dQ/dV vs SOC for cells charged at 1C and 1.5C.

Conclusions

Development and testing of higher energy, larger format cells and modules continues for USABC developers in hopes to meet the EV Everywhere 2022 goals. We provide a means to field the most inherently safe chemistries and designs to help address the challenges in scaling up lithium-ion technologies of interest. This has required careful control and monitoring of tests with the potential of high energy release as well as standing up a larger facility at SNL to support module level testing this FY. This has provided critical information to cell developers to aid in the development of increasingly abuse tolerant cell chemistries and module designs. This independent testing is also necessary to perform objective evaluations of these various designs and chemistries by the DOE and US automobile manufacturers. SNL has completed abuse testing support for all USABC deliverables to date.

The impact of varying energy contents on ARC results was explored to get a better understanding of how to consider the scaling issues around testing of smaller developmental cells. This work explored both varying states of charge as well as cells of various size. Initial work indicates there may be some limitations to the kinetics, that while the increased energy content of large cells provides more energy to thermal runaway, the heating rate will not necessarily increase as a function of cell size. The heating rate however is highly dependent upon state of charge, with elevated states of charge dramatically increasing the likelihood of high rate thermal runaway.

A study of the impact of elevated charge rate cycling was performed as a feasibility study to identify changes to abuse behavior with different charge rates and numbers of cycles. We identified a small lowering of failure SOC and a 30% drop in failure temperature during overcharge., but no effect on failure temperature during thermal ramp. We theorize that this indicates a changing cell resistance during faster charging. This thought is futher supported by dQ/dv vs SOC data showing lowered energy of a 10% SOC process and an entirely new process at 15-20% SOC in the faster charged cell. For future work, more robust cells will be used, with a goal of achieving 6C charge rates. dQ/dV will be used to identify markers of lithium plating, and possibly explain the abuse response changes seen in this work.

SNL continues to provide testing support and data to help build and validate models with other national lab partners through the CAEBAT VTO program. Additional abuse testing support for the VTO post mortem program and Si-Deep Dive expanded this year, which included overcharging cells of various chemistries

manufactured by ORNL to different states followed by posttest analysis done by ANL. Also, initial abuse testing of Si based cells has been achieved to better understand the safety impacts of this emerging chemistry.

Key Publications

1. Lamb, J. et. Al. "Consequences mitigation and detection of propagating battery failure" MRS Fall Meeting, November 2017
2. Lamb, J. et. Al. "Understanding battery safety through abusive battery testing" Energy Storage Systems Safety and Reliability Forum, March 2018
3. Lamb, J. et. Al. "Battery Safety and Abuse Testing" DOE Vehicle Technologies Annual Merit Review, June 2018
4. Lamb, J. et. Al. "Examining and Controlling the Behavior of Thermal Runaway in Multi Cell Systems" ECS Spring Meeting, May 2018
5. Karulkar, M. et. Al. "Characterization of Abuse Response during Fast Charge of Lithium Ion Batteries" ECS Spring Meeting, May 2018
6. Torres-Castro, L. "Investigations of the structural and electrochemical properties of overcharged Li-ion batteries" ECS Spring Meeting, May 2018
7. Lamb, J. et. Al. "Abuse Testing to Understand High Energy Battery Failure" AABC 2018, June 2018
8. Karulkar, M. et. Al. "Multiscale Battery Diagnostics for Improved Safety and Performance" AABC 2018, June 2018
9. Lamb, J. et. Al. "Evaluating the Impact of Initiation Methods on Propagating Thermal Runaway in Lithium-Ion Batteries" Battery Safety 2018, October 2018

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