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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). This year saw the stand up of a new drop tower tester capable of providing dynamic mechanical test results.

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. 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. To study this cells were built in Sandia's prototyping facility at varying n:p ratios, with the low n:p ratios used as conditions highly likely to plate lithium. After charging to induce lithium plating, cells were analyzed with DPA and ultimately subjected to abuse testing to observe changes in thermal runaway severity after significant lithium plating.

Objectives

- 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 high quantities of lithium plating on abuse response of cells. Evaluate control and test cells with forced lithium plating to observe the impacts to failure.
- Improve the ability of calorimetry and other test methods to withstand and provide relevant data for high energy materials, particularly their ability to withstand high temperature failure. Begin evaluations of impacts of high energy materials.
- Evaluate feasibility of using elevated temperature to render cells inert without swelling, venting or thermal runaway.
- Provide testing data to support failure propagation model (NREL)
- Provide testing support for ABR Post Test program (ORNL/ANL)

Accomplishments

- Completed testing of all USABC deliverables to date and reported results to the USABC TAC
- Inconel alloy ARC cell holders designed, built and tested
- Test cells at varying n:p ratios built in Sandia prototyping facility and cycled to induce plating in low n:p ratio cells. Cells were analyzed using DPA and abuse testing.
- Extended failure propagation modeling efforts with NREL using testing data. This resulted in newly published work using direct test data to establish validated models.
- 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)
- Boundary conditions determined for rendering cells inert. Heated cells were observed while fixed in mechanical test equipment to observe the onset and severity of potential temperature induced swelling.

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 new test development, including stand up of the drop tower, studies to render batteries inert, and testing of temperature hardened calorimetry test cells use commercial off the shelf (COTS) 18650 and pouch format cells. Generally, NMC-graphite cells were used for testing due to the general relevance to EV applications. The testing of the hardened calorimetry test cells used high energy density materials, particularly NCA-graphite cell as the cells in question had been previously observed to exhibit a severe runaway event. Testing of lithium plating effects on abusive battery failure used cells built within Sandia's battery prototyping facility to build NMC-graphite cells.

Results

Testing of deliverables was performed for USABC development programs, including testing deliverables from 24M, Amprius, Farasis and Zenlabs. Test results have been reported to the USABC Technical Assessment Committee.

Evaluations of determining if exposure to extended elevated temperature have begun with determine thresholds where cells in question will begin to excessively expand or vent from temperature exposure. This provides a threshold for the maximum temperatures that could reasonably be used to prevent excessive cell exposure. 5 AH commercial off the shelf NMC-graphite "energy" cells were used slowly ramped while clamped in a mechanical test fixture applying a constant position to the cell constraints. During this time the load cell of the mechanical test fixture was monitored for the onset of significant swelling. Figure 1 shows the results of this initial testing. In this cell, we observed constant cell pressures until the cell temperature exceeded 100 ˚C. Above this temperature, a rapid increase in cell pressure was observed until the cell ultimately went into thermal runaway. The voltage with respect to temperature is shown in Figure 2 and this shows that some voltage drop was observed at moderately elevated temperatures as well. This presents the possibility for a high temperature induced accelerated self-discharge that could be used to render batteries inert for transport to final disposition.

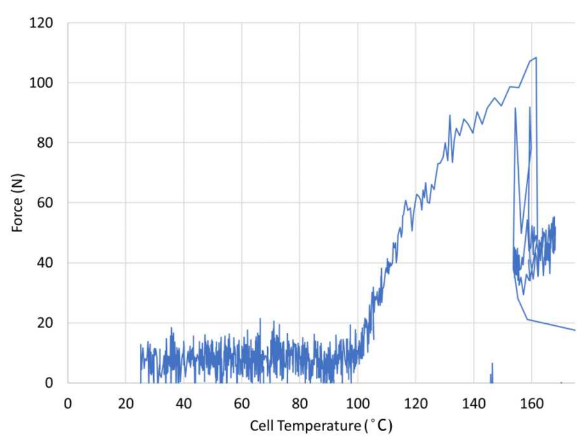

Figure B.3.1 Force against mechanical test apparatus of a cell fixed in place within the test fixture as temperature is increased. Used to evaluate cell swelling, this shows little to no swelling up to 90-100 °C. Above this the force begins to rapidly increase until venting occurs at ~150 ˚C

New trends in battery development have largely focused on the development of high energy density materials, including silicon anode materials, high nickel content cathode materials and solid state batteries to enable lithium metal rechargeable batteries. The high energy density of these cells has exposed limitations in the traditional materials used to measure and contain battery failure during abuse testing. Modifications of capabilities have been performed to better support testing of high energy anode and cathode materials. In particular, increased temperatures have been observed during thermal runaway that have damaged test equipment and exceeded monitoring capabilities. Accelerating Rate Calorimetry hardware has been modified to include high temperature alloy cell holders to replace the stainless steel holders previously used. These were tested and able to withstand a high rate runaway from a 3.1 AH NCA-graphite cell that had previously damaged a stainless steel holder. This provides the capability for planned ARC testing of silicon anode cells to better understand its role in thermal runaway. Modular data acquisition devices capable of high temperature thermocouple inputs have also been aquired to stand up high temperature thermocouple measurements for future testing and better understand the maximum potential temperatures that are occurring in general abuse tests.

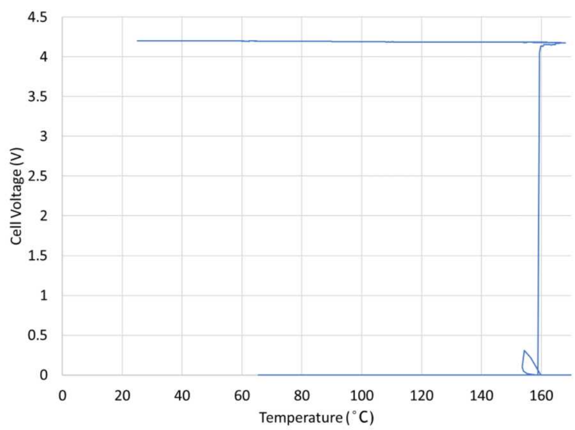

Figure 0.1 Voltage vs temperature of cell tested in Figure 1 above. A slight drop in voltage is observed with increasing temperature, indicating potential feasibility of rendering the cell inert through self-discharge over time. Voltage rapidly drops to 0 when cell failure occurs.

The primary objective of the lithium (Li) plating project is to observe the effect of varying amounts of lithium plating on the safety characteristics of lithium-ion (Li-ion) cells subjected to abusive conditions. To satisfy this underlying goal, the following three objectives have been proposed: (1) Develop a method for preferentially plating Li metal on a graphitic anode, (2) Investigate the effect of Li plating on cell safety characteristics during abusive conditions, and (3) Investigate the effect of C-rate on extent of Li plating/stripping and its effect on abuse response. To eliminate variability in our results, we are utilizing a cradle-to-grave approach which includes fabrication of 1Ah pouch cells using in-house electrode and electrolyte formulations. Cell cycling schedules are consistent between cells, as are parameters during abuse testing. The use of high-rate cycling has been utilized to preferentially plate Li on anodes with variable n:p ratios. Two sets of cells have been fabricated, of which one was deconstructed to visually inspect for Li plating and the other subjected to abuse cycling. Cell teardowns (see below image) suggest that extent of Li plating scales with decreased n:p ratio. Initial results from overtemperature testing indicates that greater extent of Li plating leads to exacerbated abuse response, where cells with 1.2 and 0.75 n:p ratios failed to exhibit runaway behavior even at high temperatures (>250°C). On the other hand, the 0.5 n:p ratio cell exhibited a violent runaway reaction at ~130°C. All cells exhibited pouch bulging and subsequent venting, however it is speculated that the additional Li plating present in the 0.5 n:p ratio cell was the primary factor leading to exacerbated abuse response (see below image).

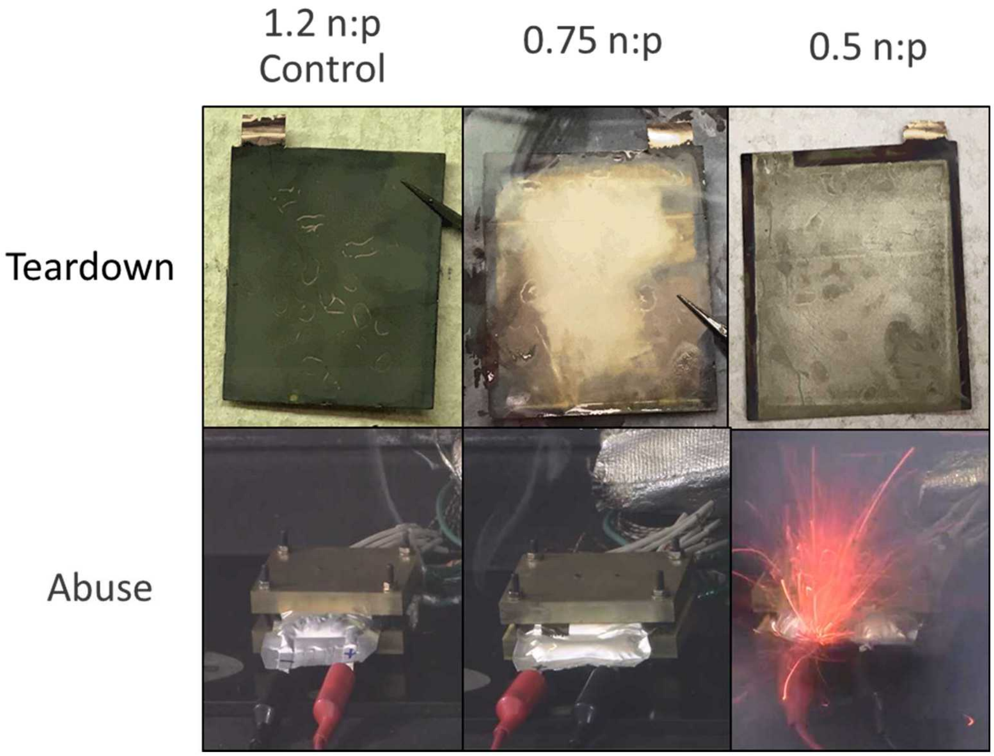

Figure 0.3 DPA and abuse test behaviors of cells with reduced n:p ratios to force significant lithium plating. Visible deposits are observed in the low n:p cell, with a significant thermal runaway event observed.

Continued research will involve subjecting cells to a greater array of abuse tests relevant to vehicle battery packs, including mechanical crush, overcharge and accelerated rate calorimetry (ARC). Work is also being conducted to determine whether a Li plating plateau exists beyond which exacerbated abuse response will not persist. Finally, a modified cycling schedule which involves higher rate cycling will be implemented to determine the dependence of C-rate on the safety performance of test subjects.

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.

Work has been performed this FY to expand the capabilities at SNL. A drop tower impact tester has been developed to better understand how batteries fail under dynamic loading conditions in collaboration with the CAEBAT program. Cell holder equipment for accelerating rate calorimetry has also been temperature hardened to better accommodate the high temperature failures that have been observed with high energy active materials. On going testing will evaluate the impact of increasing levels of silicon in the failure response of 18650 cells. Work is also on going to provide better detection of high temperature failures during standard abuse tests.

Low n:p ratio cells were built to force lithium plating on test cells and evaluate the impact of lithium plating on abuse response. The low n:p cells were shown through DPA to have significant lithium plating after cycling. This also resulted in a more severe abuse response in the low n:p cells that included a significant thermal runaway in the 0.5 n:p cell. This included ejection of incandescent particles and self-ignition of the vent gasses. Higher n:p ratios did not show a significant thermal runaway event in the cells tested.
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. Preparations have been made as well to provide support to safety critical tests that may develop as the result of cell recycling efforts.

Key Publications [Use EERE Heading 3]

1. Q. Li, C. Yang, S. Santhanagopalan, K. Smith, J. Lamb, L. A. Steele, L. Torres-Castro, “Numerical investigation of thermal runaway mitigation through a passive thermal management system,” Journal of Power Sources, vol. 429, p.p. 80, 2019
2. Lamb, J. et. Al. “Evaluating the Impact of Initiation Methods on Propagating Thermal Runaway in Lithium-Ion Batteries” Battery Safety 2018, October 2018
3. Lamb, J. et. Al. “Mechanisms and Material Impacts of Overcharge in Lithium-ion batteries” MRS Fall Meeting, November 2018
4. Lamb, J. et Al. “Evaluating the Impact of Initiation Methods on Propagating Thermal Runaway in Lithium-Ion Batteries” SAE Government Industry Meeting 2019, March 2019
5. Lamb, J. et Al. “Scaling Accelerating Rate Calorimetry Results” Spring Meeting of the Electrochemical Society, May 2019
6. Torres-Castro, L. et al., Mechanisms and material impacts of overcharge in lithium ion, 235th ECS Meeting, Dallas, Texas; May 26-30, 2019
7. Karulkar, M. et al. “High Precision Characterization of Li-Ion Batteries during Extreme Fast Charging” 235th ECS Meeting, Dallas, Texas; May 26-30, 2019
8. Lamb, J. et Al. “Failure Propagation Work and Abuse Testing” Advanced Automotive Battery Conference, June 2019
9. Karulkar, M. et Al. “Characterization of Abuse Response during Fast Charge of Lithium Ion Batteries” Advanced Automotive Battery Conference, June 2019
10. Lamb, J. et Al. “Evaluating the Impact of Energy Density on Thermal Runaway” Battery Safety Summit 2019, October 2019
11. Lamb, J. et Al. “Battery Safety and Abuse Testing Overview” Stanford Battery Seminar Series, October 2019
12. Stanley, J. et al. “Li-ion Battery Impact Testing” AMSE InterPACK Conference, October 2019
13. Deichman, E. e al. “Analyzing the effect of lithium plating on the safety performance of lithium-ion batteries” Fall ECS Meeting, October 2019

Acknowledgements [Use EERE Heading 3]

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