Characterizing the Safety of Commercial Sodium-ion Cells and Modules

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1 Introduction

Global energy needs have rapidly increased in recent years, leading to a higher demand for stationary energy storage from utilities, data centers, warehouses, etc. This demand has driven the need for reliable and cost-effective large-scale storage solutions. While lithium-ion batteries (LIB) have been the primary choice due to their high energy density and long cycle life, the growing demand across multiple industries has prompted manufacturers to seek alternatives [1]. Sodium-ion batteries (SIB) have emerged as a viable option, particularly for stationary storage applications. The abundance of raw materials and similar manufacturing processes to LIBs make SIBs a cost-effective solution for mass production [2-4].

Stationary storage systems can vary in size depending on the application, from a few kilowatt-hours to several megawatt-hours in stored energy. However, numerous failure incidents leading to fire and thermal runaway have occurred at stationary storage facilities using lithium-ion batteries in recent years [5]. Several individual cells are connected in a series-parallel configuration to make a battery module, and numerous such modules are used in battery energy storage systems [6]. A failure at the cell level could easily cascade into a catastrophic event at the battery system level. Therefore, understanding a cell's thermal safety and hazard characteristics is vital.

Here, results have been reported from safety studies conducted on commercial sodium-ion cells from two different manufacturers. For this study, two different capacities of 18650 sodium-ion cells (1.2 Ah and 1.5 Ah) were investigated. All cells were comprised of layered transition metal oxide cathode materials. To understand the cells' safety characteristics, we performed a series of tests, such as overcharge, over-discharge, external short, and external heating tests. Mini-modules with three cells in series were also built and tested. This manuscript includes only the external heating tests at the mini-module level.

2 Experimental Details

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Two different manufacturers of commercial 18650 sodium-ion cells with rated capacities of 1.2 Ah (Manufacturer A) and 1.5 Ah (Manufacturer B) were investigated. Table 1 below provides specifications of the test samples. The following safety tests were performed at the cell level: (i) overcharge, (ii) overdischarge, (iii) external short, and (iv) external heating. A total of 30 cells (15 from each manufacturer) were used for the tests, and each safety test was repeated thrice.

Subsequently, safety tests were conducted using 12V (3 cells in series) mini-modules. A series of safety tests were conducted on the mini-modules. Cells from the two different manufacturers were not mixed to make the mini-modules. As a part of this document, results from tests involving external heating will be discussed.

All safety tests were performed in an explosion-proof chamber, where voltage, current, and temperature signals were monitored, and real-time videos were captured. Although tests were repeated on multiple samples to gain better insight and for statistical understanding, only results from the most extreme cases of each test are compared in this manuscript. In subsequent sections, the word "Manufacturer" is abbreviated as "Mfr."

Table 1: Specifications of sodium-ion test samples

Cell Specification	Manufacturer A	Manufacturer B
Cell Format	18650	18650
Rated Capacity (mAh)	1210	1500
Measured Capacity (mAh)	1208	1560
Internal Resistance (mΩ)	75.1 (measured)	58.7 (measured)
Weight (g)	36	37.2
Max voltage (V)	3.95	4.1
Min Voltage (V)	1.5	1.5

3 Results and Discussion

The next few sections provide results and observations for cell-level and module-level tests conducted.

Overcharge test – Cell Level: Figure 1 shows the voltage, current, and temperature response of an overcharge test conducted on individual cells from both manufacturers. The overcharge test was conducted with a current of 1C and a voltage limit of 12 V. During the overcharge test, cell from Mfr. A showed a voltage spike when charging beyond 6V, whereas for Mfr. B cell voltage spike occurred at ~5.6V. In the case of Mfr. B, after the cell voltage spiked to 12.9 V, there was continuous voltage fluctuations, and the temperature rose up to ~90ºC. Electrolyte venting from the cell was also observed. After the overcharge test, the tested cells from both Mfr. A and B that did not undergo electrolyte venting were subjected to a discharge but they did not accept the load, and they could not be charged either. . Upon further inspection by conducting destructive physical analysis (DPA) of the cell, it was observed that the current interrupt device (CID) in the cell header was activated, resulting in the cells becoming open circuit.

Overdischarge test – Cell Level: During the overdischarge tests, cells from Mfr. A could continue to be discharged until the capacity reached 150% of the rated capacity from 0V without experiencing any failure. However, the cell from Mfr. B could not be discharged beyond 31 minutes. During the test, cell voltage jumped to a higher voltage value when prolonged overdischarge was attempted, indicating that it could be a benign internal short circuit. Cells from Mfr. A were able to hold current for a longer period. It is worth noting that no off-nominal events were observed during these tests for the cells from both Mfr. A and B. However, the cells were unable to take charge after the overdischarge tests indicating that the cells had undergone benign short circuits under the overdischarge condition they were subjected to. Figure 2 shows the voltage, current, and temperature data from a single overdischarge test conducted using individual cells from each manufacturer.

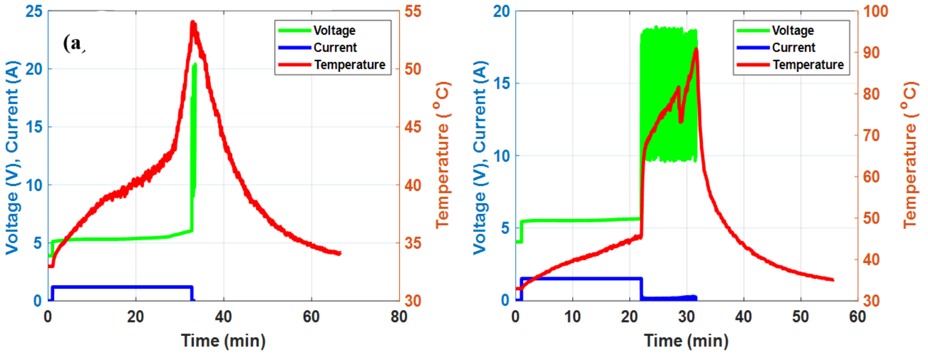

Figure 1: Measured voltage, temperature, and current response for the overcharge test on the cells from 2 manufacturers: Left: Manufacturer A and Right: Manufacturer B. Cell from manufacturer B resulted in venting a few minutes after the sudden increase in voltage with the corresponding temperature rise.

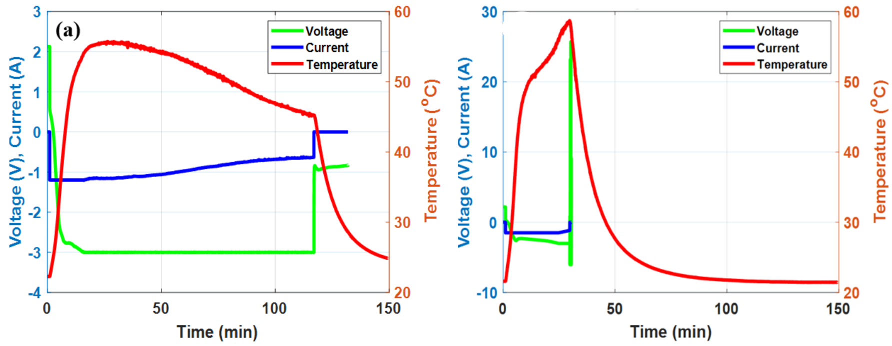

Figure 2: Measured voltage, temperature, and current response for the overdischarge test Left: Manufacturer A, Right: Manufacturer B. Cell from manufacturer B failed sooner than the cell from manufacturer A. Peak temperatures of both the cells are below 60 ºC.

External short tests – Cell Level: Tests were performed at 50% and 100% states-of-charge (SOC). To induce a hard short, an external resistance of ~10 mΩ was used. For Mfr. A cell at 50% SOC, peak current of 8 A was observed, whereas for 100% SOC, it was 12.6A. Further, during the 50% SOC test, a peak temperature ~48 ºC was observed, and for the 100% SOC case, it was higher (~65 ºC), which can be expected as the cell has higher stored energy at 100% SOC than 50% SOC. Results from the same tests on Mfr. B cells showed that the peak current for 50% SOC case was nearly double that of manufacturer A cell at ~15.9A. Also, the temperature of the cell reached ~56 ºC. For the 100% SOC condition, the peak current was significantly higher for Mfr. B when compared to the Mfr. A cell at 34 A. Figure 3 shows the voltage, current, and temperature of the cells. None of the cells displayed any off-nominal events during this test.

External heating test – Cell Level: Cells during this test were at 100%SOC and heated using Kapton tape heater at 10ºC/minute ramp rate. Cell from Mfr. A subjected to the external heating test experienced thermal runaway with peak temperature rising to 305 ºC. The onset of thermal runaway occurred at 149 ºC. Fire was observed for this test, and some of the cell contents were ejected. Similarly, Mfr. B cell also experienced thermal runaway due to external heating. A peak temperature of 450 ºC was observed, with the onset of thermal runaway occurring at 139 ºC. The onset of thermal runaway for Mfr. B cell occurred slightly earlier than the Mfr. A cell. The contents of the cell from Mfr. B were completely ejected, which indicates a more energetic explosion when compared to the Mfr. A sample. All the cell samples that underwent external heating resulted in thermal runaway. Figure 4 shows the data signals that were collected during one of the tests. Figure 5 shows the pre- and post-test images.

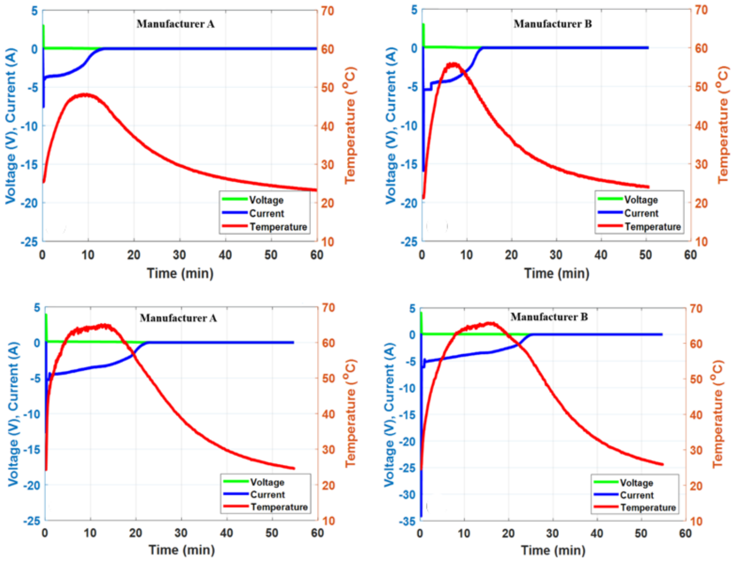

Figure 3: Measured signals during the external short test. at 50% and 100% SOC. Top: Cells at 50% SOC, Bottom: Cells at 100% SOC

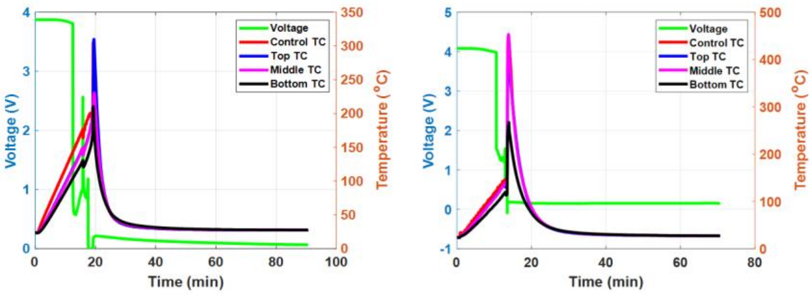

Figure 4: External heating test results Left: Manufacturer A, Right: Manufacturer B

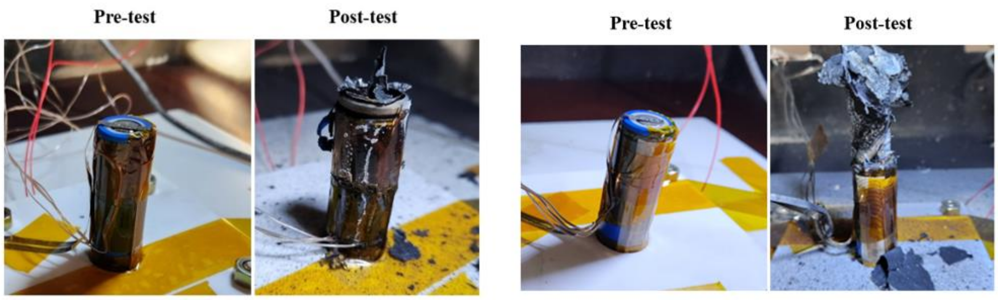

Figure 5: Pre and post-external heating tests Left: Manufacturer A, Right: Manufacturer B

External heating test – Module Level: This test was conducted only for Mfr. B module by externally heating the middle cell using Kapton tape heater at 10ºC/minute ramp rate. All the cells were charged to 100% SOC before the test. During this test, the onset of thermal runaway occurred at ~188 ºC, and the maximum temperature was observed to be 325 ºC. There was no thermal runaway propagation during this test. Figure 6 shows the voltage, time, and temperature of the module. During this test, the gases released during thermal runaway were collected using a gas canister and subsequently analyzed using gas chromatography-mass spectrometry (GC–MS). It was observed that the gases contained many organic compounds that are harmful at very small percentages, including hexene, benzene, toluene, etc. Percentages of gases in the collected sample are provided in Table 2. Gases such as N_2, CO_2, O_2 and others less than 0.1% are not included.

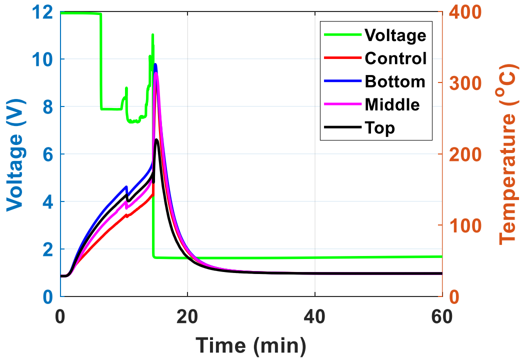

Figure 6: External heating test result of the module from Manufacturer B

Table 2: Components and percentages from the collected gas sample of Mfr. B module from the external heating test

Component	Percentage (%)
Carbonic Acid, dimethyl ester	31.30
Carbon Monoxide	28.20
Hydrogen	18.80
Carbonic Acid, ethyl methyl ester	8.55
Ethylene	4.22
Methane	2.82
Propylene	2.44
Ethane	0.54
Methyl Acetylene	0.53
Hexene	0.50
Benzene	0.39
Propadiene	0.23
Propanal	0.20
Propane	0.16
Styrene	0.15

Acetaldehyde	0.15
Difluromethane	0.14
Toluene	0.10

4 Conclusion

Cell-level safety tests on commercial 18650 sodium-ion cells from two different manufacturers were performed to understand the thermal stability and behavior of the cells under different abuse scenarios. The external short tests were conducted at two different SOC's to understand the influence of SOC on cell behavior during this abuse condition. One of the manufacturer B cells did exhibit venting behavior during overcharging. All the cells that were subjected to external heating resulted in thermal runaway. In addition, external heating test on the sodium-ion module (during which a heater was installed on a single cell) resulted in thermal runaway of the cell on which the heater was installed, but no propagation was observed from cell to cell. Based on the results from the safety tests, it cannot be claimed that sodium-ion cells are safer than lithium-ion cells. The results from the study show that safety improvements are still needed for sodium-ion cells before deploying large-scale storage systems.

References

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