Safety and Performance Testing of Commercially Available Sodium-ion Batteries

Rachel Carter[1], Gordon Waller[1], and Corey T. Love[1]

[1]*Alternative Energy Section (Code 6173), U.S. Naval Research Laboratory, Washington, DC, USA*

ABSTRACT: Sodium-ion batteries (SIBs) have emerged on the global market and are poised to complement the ubiquitous Li-ion battery (LIB). SIBs deliver a lower energy density compared to LIBs but utilize more globally abundant materials and boast a higher degree of safety. The cell safety comes from less reactive cathode materials, lower cell energy density, and, in some cases, less flammable electrolytes. SIBs function much like the LIBs but with larger alkali ions. However, material compatibility distinct from lithium results in a wide range of active and passive materials present in SIBs. The wide range of material components make safety risk assessment difficult. Herein we assess safety of two commercial prototype SIBs; one aqueous and one non-aqueous with accelerating rate calorimetry and electrochemical analysis. The safety and electrochemical stability of these cells are then compared with commercial Li-ion battery chemistries. The aqueous and non-aqueous SIBs utilize aluminum metal foil for both positive and negative current collectors since sodium and aluminum do not alloy. This is a unique feature in comparison to LIBs which require a copper current collector at the negative electrode, preventing low voltage storage, where the copper reduces and dissolves. Therefore, we investigated "de-energized" or 0 V storage of both SIBs. The aqueous proved robust to these excursions, while the non-aqueous exhibited capacity loss but maintained a high degree of safety.

Keywords: Sodium ion battery, Na-ion battery, safety, accelerating rate calorimetry, 0V storage, safety

Introduction

The demand for lithium-ion batteries (LIBs) is steadily increasing and their material supply chain is of growing concern. Sodium-ion batteries (SIBs) operate mechanistically similar to LIBs but deliver lower energy density. In the 2010s, SIB companies were incentivized to address niche needs like grid storage and load leveling. More recently, commercial SIBs have emerged from these companies, boasting safety and high-power capability.

Among commercial LIBs, the cathode type may vary, but the anode and electrolyte differ very little. However, SIBs have different material compatibilities than LIBs and shuttle a larger ion. Therefore, a wider range of active and passive material components are used among the few (<10) SIB companies. For example, anodes may be hard carbon, alloying material, or intercalation materials; electrolytes may be aqueous or non-aqueous. This makes safety and performance generalizations about the chemistry difficult. Here we compare an aqueous and non-aqueous SIB.

Quantitative and qualitative comparisons of failure modes for aqueous and non-aqueous SIBs are assessed with accelerating rate calorimetry. This adiabatic assessment allows for measurement of onset temperature of self-heating behavior, calculation of heat release during thermal runaway, and visual inspection of the failure mode. Using our prior art, we can compare our findings for aqueous and non-aqueous commercial SIBs to commercial LIBs.

Additionally, a benefit of the different material components of SIBs is the use of Al current collectors at both electrodes. Sodium does not alloy with aluminum, like lithium does. LIBs require use of a Cu anode current collector which, prevents 0V storage due to Cu dissolution, which would compromise performance and safety. Therefore, SIBs can be stored in a "de-energized" or 0V state.

Methods

Accelerating rate calorimetry (ARC) was used to characterize thermal stability behavior and assess cell safety[1] (Thermal Hazard Technology, UK). This measurement allows calculation of peak heat rates (W and °C/min), peak temperature, and chemical energy of the electrochemical system (heat of reaction). We employ a heat-wait-seek (HWS) testing methodology whereby a thermocouple instrumented cell is "heated" in 5 °C increments, the chamber "waits" for equilibrium (40 min) and "seeks" for self-heating or heating of the test article any rate beyond a threshold of 0.02 °C/min. If self-heating is not detected the calorimeter continues to the next 5 °C increment.[2] When self-heating is detected, the chamber approximates adiabatic conditions by maintaining the temperature chamber as close to the self-heating rate of

the cell as possible. For battery thermal runaway this test is effective and adiabatic except in the regions where cell-venting and peak heat rates are observed. A cell is considered to be in thermal runaway when the heat rate surpasses 5 °C/min. For reference, Li-ion cells often surpass a maximum self-heating rate of 1000 °C/min.[2]

Two commercial Na-ion cell types were assessed: one aqueous (pouch type, 4.3Ah, 1.2-1.8 V) and one non-aqueous (18650, 0.7 Ah, 2-4.2 V). Both cells were tested in a fixtured apparatus which replicates a single cell situated with neighbors and experiencing thermal runaway.

Electrochemical assessment of cell capacity, rate capability and 0 V tolerance were assessed using MACCOR Series 4200 and Series 4000 cyclers. Environmental chambers were used to assess various ambient thermal environments.

Results and Discussion
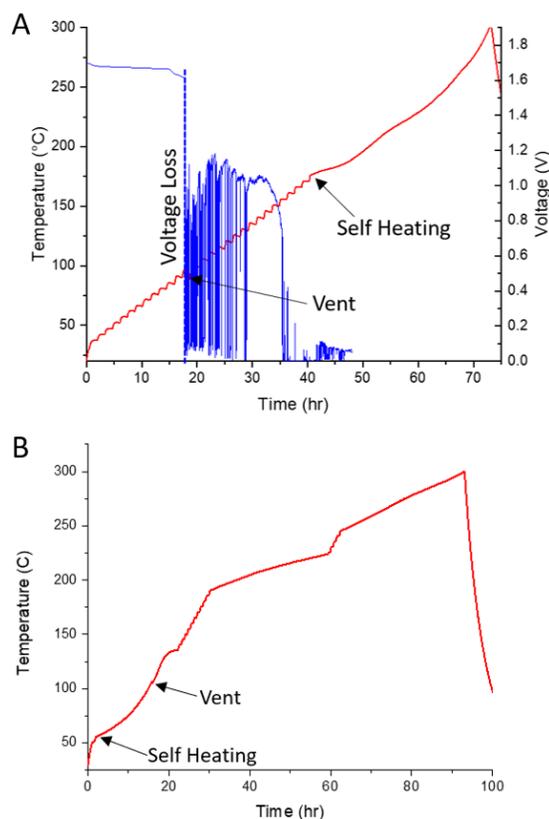
Figure 1- Heat-Wait-Seek ARC measurement of (A) aqueous and (B) non-aqueous SIBs.

Heat-wait-seek test of the aqueous cells, which are a large pouch form factor, were completed in the ARC EV. The fixtured aqueous cell (Figure 1 A) experiences voltage loss and venting at about ~100°C, however self-heating is not detected until ~175°C. This is a demonstration of heat rejected into the cell fixture, reducing self-heating. We designed a cell fixture of approximately the same mass as the aqueous cell, ~290 g. This mimics a neighboring cell in a pack.

Accelerating rate calorimetry data for the non-aqueous SIB is given in Figure 1B. After the onset of self-heating, a vent is observed between 110-120 °C. This temperature is similar to the onset of self-heating observed in conventional Li-ion cells, likely due to similar volatile solvents used for the battery electrolyte.[2, 3] These solvents are vented off by a pressure release. After the vent, low self-heating is observed until the components are burned and the samples are cooled down at a safety temperature of 300 °C.
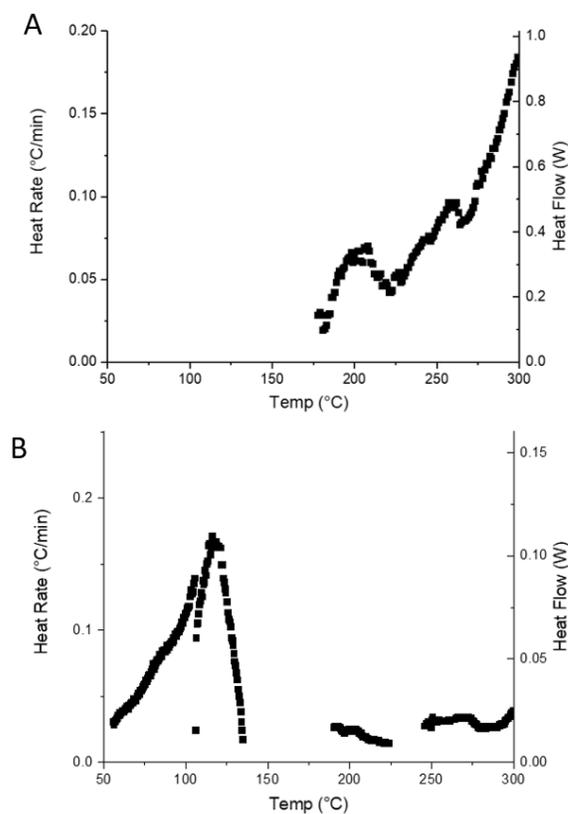
Figure 2- Heat-rate or heat flow measured in self-heating regimes of aqueous (A) and non-aqueous (B) SIBs.

The self-heating regimes of the HWS measurements in Figure 1 are manipulated into heat rate vs. temperature plots, which are often used to compare safety among cells. For the aqueous cell (Figure 2A), self-heating is not observed until ~175 °C and remains minimal (<1 W) in up to the safety temperature of 300°C. However, the non-aqueous cell (Figure 2B) exhibits a notably low onset temperature of ~50 °C, but the heat rates remains low (< 0.2 °C/min and 0.2 W). In practice, this heat would easily dissipate to neighboring cells or packaging when assembled into a pack.
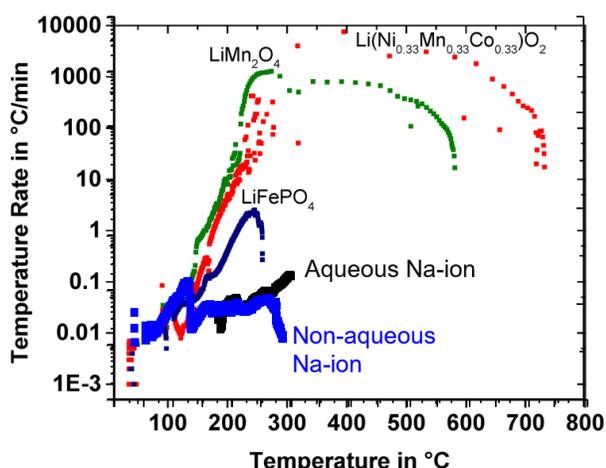
Figure 3- Temperature rate with respect to temperature in self-heating regimes of conventional LIB cells and SIB cells investigated here.

To put our observations on SIBs into context, the SIB heat rates are overlayed with commercial LIB data for various cathodes (Figure 3). Both the aqueous and non-aqueous SIBs have temperature rates far below that of LIBs. A threshold of ~5 °C/min indicates thermal runaway, which is observed for all LIBs but neither SIB.

A notable quality of SIBs is the elimination of the copper current collector, which allows for safe 0 V or 0% SOC storage. Figure 4A shows cell cycling data within the manufactured recommended voltage range (1.2 – 1.8 V) with additional periodic excursions to 0 V, 0% SOC. On the 5th cycle the cell was discharged to 0 V and rested for 5 hours. Minimal degradation was observed over this protocol, even after twenty 0 V excursions for a total of ~100 cycles (Figure 4B).
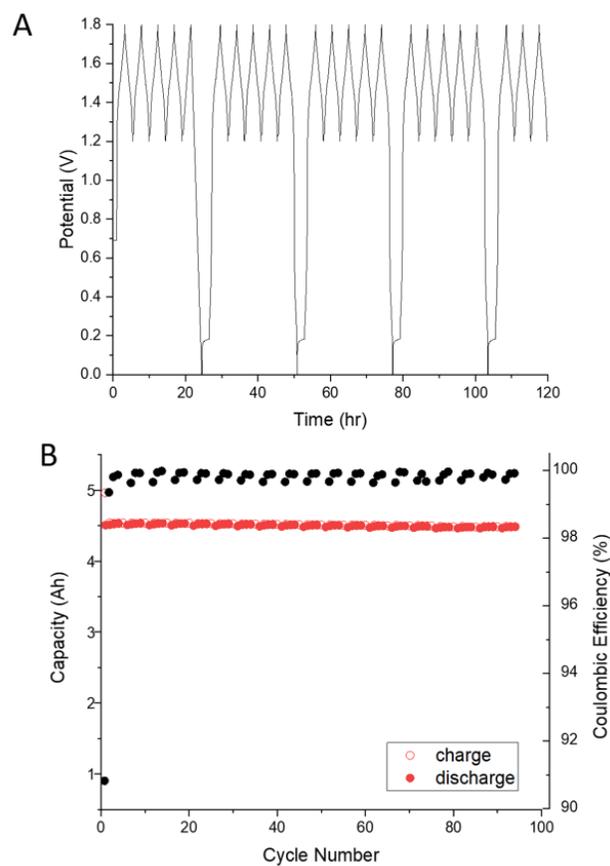
Figure 4- 0V excursions every 5 cycles on aqueous SIB

The 0 V capability of the non-aqueous cells was examined in a similar manner: 4 cycles in the conventional voltage range (2- 4.2V) followed by a 5th cycle with discharge to 0 V and a 5-hour rest (Figure 5A). In contrast to the aqueous cells, the non-aqueous cells exhibited capacity loss after discharging to 0 V. After only six repetitions of this test, 15% capacity loss was observed (Figure 5B), revealing degradation to the cells.

Capacity degradation has been associated with compromised cell safety in LIBs.[4] Therefore, we completed HWS assessment of the non-aqueous cell degraded by 0V excursion. At the same state of charge as the pristine non-aqueous cell from Figure 1B and Figure 2B, the degraded cell demonstrated a similar HWS test response. This indicated that, the capacity loss due to 0 V hold did not translate into compromised safety of the non-aqueous SIB.
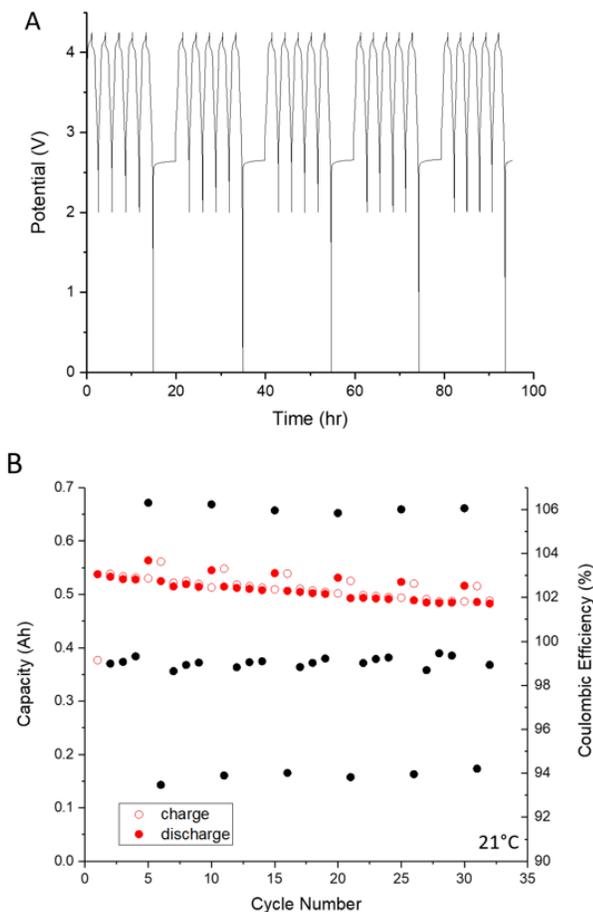
Figure 5-0 V excursions every 5 cycles on non-aqueous SIB

Conclusions

The failure modes of two sodium-ion batteries, one with aqueous electrolyte and one with non-aqueous electrolyte were assessed with accelerating rate calorimetry. Neither cell type exhibited thermal runway or catastrophic failure. Both cells deliver low (<5 W) heat release attributed to material combustion. The aqueous cell delivered the most benign failure, likely since it has a non-flammable electrolyte and low energy density (22 Wh/kg). The aqueous cell is a large pouch cell, allowing seal breaching from electrolyte vaporization at ~100 °C and does not exhibit self-heating until temperatures >150 °C. The peak heat rate during component combustion was 0.18 °/min or 2 W of heat flux.

The non-aqueous cell has a higher energy density (77 Wh/kg) and contains flammable electrolyte. This cell exhibits self-heating at milder temperatures, 55 °C. Cell venting occurs around 100 °C when electrolyte is ejected from the cell leading to a peak heat rate of 0.1 °C/min or 0.12 W.

An advantage of SIBs over LIBs is the ability to store cells in a de-energized state, 0 V or 0% SOC. We examined the influence of 0 V storage on safety and performance for both the aqueous and non-aqueous cells. aqueous cells remained robust to 0 V storage and cycling. No degradation was observed. The non-aqueous cells exhibited capacity fade after 0 V storage, indicating degradation to the cell. However, when subjected to ARC testing the non-aqueous cells degraded by 0 V storage delivered similar failure modes to pristine non-aqueous cells, indicating the degradation does not impact safety.

References

(1) Klein, E. J.; Carter, R.; Love, C. T. Accelerating Rate Calorimetry and Complementary Techniques to Characterize Battery Safety Hazards. *J Vis Exp* **2021**, (175). DOI: 10.3791/60342 From NLM.

(2) Lei, B.; Zhao, W.; Ziebert, C.; Uhlmann, N.; Rohde, M.; Seifert, H. J. Experimental Analysis of Thermal Runaway in 18650 Cylindrical Li-Ion Cells Using an Accelerating Rate Calorimeter. In *Batteries*, 2017; Vol. 3.

(3) Peters, J. F.; Peña Cruz, A.; Weil, M. Exploring the Economic Potential of Sodium-Ion Batteries. *Batteries* **2019**, *5* (1), 10.

(4) Carter, R.; Klein, E. J.; Atkinson, R. W.; Love, C. T. Mechanical collapse as primary degradation mode in mandrel-free 18650 Li-ion cells operated at 0 °C. *Journal of Power Sources* **2019**, *437*, 226820. DOI: https://doi.org/10.1016/j.jpowsour.2019.226820.