A Standardized Testing Framework for Baselining & Benchmarking Pre-commercial Lithium-ion Cells

***Dillon Hayman*[2] *and Corey Love*[1]**

[1]Chemistry Division
U.S. Naval Research Laboratory
4555 Overlook Ave SW, Washington, DC 20375
corey.love@nrl.navy.mil

[2]Excet Inc
6225 Brandon Ave #360, Springfield, VA 22150

Abstract: *A testing methodology for unbiasedly benchmarking and comparing emerging and existing battery technologies is presented. Each step of the testing process is described in general terms along with the motivation for the test design. Additional information about the testing procedures can be found in the Naval Research Laboratory Battery Test Manual for Baselining & Benchmarking Pre-commercial Cells*[1]*. Experimental data produced by following the steps in the testing framework is presented and explored for a few selected procedures. As more cell-types are examined, further revisions and expansions to these methodologies are intended.*

Keywords: battery testing; Lithium-ion batteries; 18650; Sodium-ion batteries; battery characterization; rate study; cycle life; calendar life

Introduction

Modern batteries are available in a wide array of chemistries and form factors. The varied nature of available cell-types creates a diverse energy storage landscape with each set of cell construction parameters exhibiting specific strengths and weaknesses. Generally, the benefits of one cell-type will also come with a set of weaknesses such as an increase in energy density, but a decrease in cycle life. However, in many cases cell performance metrics are more complex to characterize and require a full spectrum of testing to provide a complete description of the technology. Additionally, if the testing framework is not intelligently designed to remove bias towards any cell-type, then comparisons can be difficult to make even with a full-spectrum of tests. Due to these challenges, there is a need for a standardized, rigorous testing framework that can be used to draw unbiased conclusions about advantages and disadvantages of each cell-type. After a neutral profile is created, each unique technology can be applied to a need which matches its performance parameters enabling greater and faster utilization of existing and emerging technologies. Although other high-quality battery testing methodologies exist[2,3,4], most focus on testing procedures specifically catered to electric vehicle applications. In other cases, the testing design is too simplified to be replicated exactly in separate laboratories and battery testing centers. This testing methodology aims to provide a detailed description of testing procedures such that unaffiliated battery testing locations can follow the outlined steps and arrive at the same conclusions. When battery data is easily comparable, benefits of emerging technologies can be quickly identified, even when testing occurs at a different testing center. Additionally, the procedures in this framework are well-suited to characterizing pre-commercial cells for which there are limited rigorous testing methods publicly available. Testing procedures within this framework were inspired by an amalgamation of previous testing methods designed by the United States Advanced Battery Consortium[3], Federal Consortium For Advanced Batteries[2] and Idaho National Laboratory[4] combined with battery research expertise from the Naval Research Laboratory.

Experimental

High energy 18650 lithium-ion and pouch cell sodium-ion cells were tested in this work. Cells were charged and discharged using Maccor Series 4000 and Series 4300 battery cyclers. During all steps of testing, the ambient temperature was controlled to a desired setpoint within a +/- 2°C tolerance. Temperature control was accomplished using Maccor EV chambers and Tenney environmental chambers. 18650 cells were connected to the testers using Maccor 18650 holders and Anderson connections. Pouch cells were connected to the testers via Anderson connectors with the electrode tabs contacted by a screwed down copper bar. Data was collected at an interval of every 2 mV or 30 seconds.

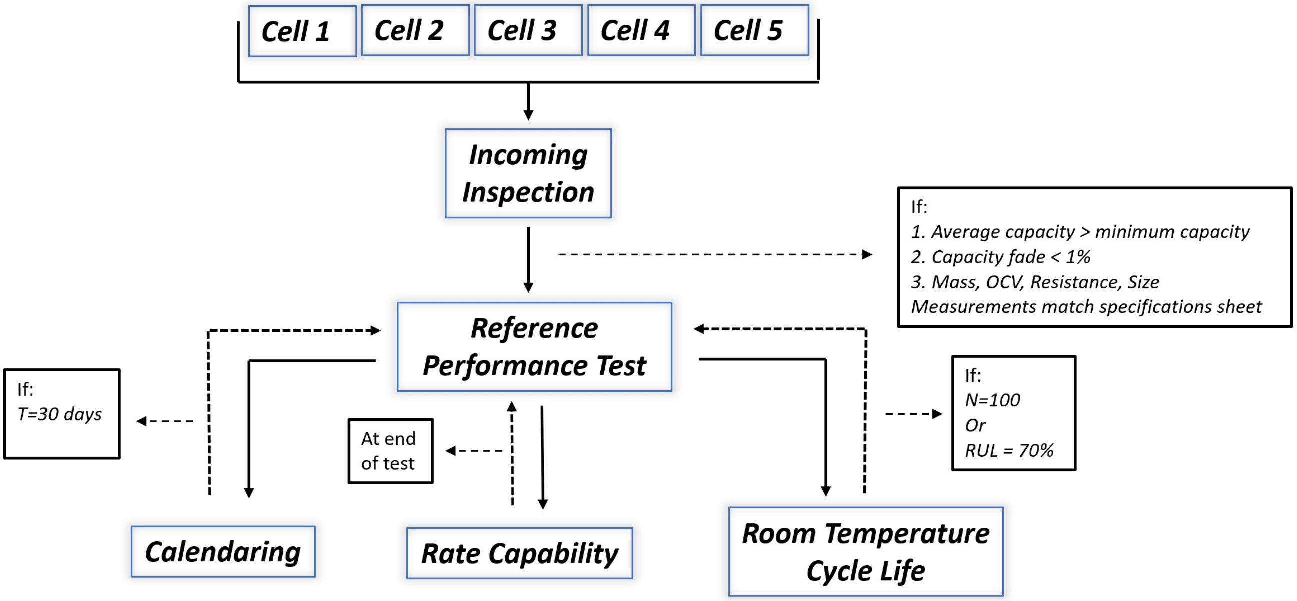

Figure 1. Battery Testing Framework Schematic

Testing Framework

Battery testing generally falls into 3 broad categories: Cycle life, rate capability and calendar life. At the beginning and at regular intervals throughout testing, reference performance tests (RPTs) are conducted to establish a baseline and measure changes in relevant parameters. However, prior to general testing, a set of incoming inspection procedures must be performed to ensure any outliers or damaged cells are removed from the batch before testing. The flow of procedures for a sample of cells is shown in **Figure 1**. In the first phase of the incoming inspection, physical and electrical parameters such as mass, open-circuit voltage (OCV), resistance and cell dimensions are compared with the cell manufacturer's specifications sheet and used to screen out cells if any criteria is not met. After cells pass through the initial set of measurements, 3-10 cycles are performed using cycling parameters from the manufacturer's specification sheet. In general, specifications sheets will contain information about standard cycling voltages and rates for charge and discharge. In cases where cycling information is unavailable, a C/2 charge to the upper voltage limit combined with a C/20 current cut-off can be used in conjunction with a C/5 discharge. Additionally, a one-hour rest should always exist between the charge and discharge. Once a set of 3 cycles records a discharge capacity within +/- 1% for those 3 cycles, cycling is stopped. From those 3 cycles, an average capacity is calculated for each cell which is compared with the rated capacity on the manufacturer's specifications sheet. If a cell cannot achieve stability within 10 cycles or record an average discharge capacity greater than the rated minimum, then the cell is excluded from further study. Following inspections, batches of screened cells are baselined using an initial RPT. After the baseline RPT is completed, the cells can move on to each of the 3 tests. Each test should be conducted using a minimum of 5 cells in each batch. Additionally, a batch of cells used in one test should not be used in another. A minimum of 15 cells is required to complete all tests in this framework. However, greater insights can be elucidated if a higher number of cells are available for testing.

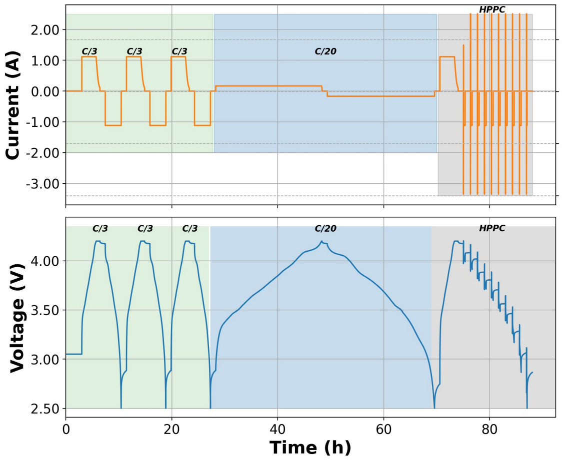

Figure 2. Reference Performance Test Current Profile and Representative Voltage Response

Prior to each test, one RPT should be completed as a baseline. RPTs consist of 3 cycles with a rate of C/3, 1 cycle with a rate of C/20, and 1 set of Hybrid Pulse Power Characterization (HPPC) measurements following a standard charge. A schematic of the current, C-rate and voltage during an RPT is shown in **Figure 2**. Additionally, it is critical that each RPT is performed at 25°C to remove any temperature effects. The initial 3, C/3 cycles serve as a benchmark for comparison of cell cycling behavior under mild conditions. The C/20 slow-cycle characterizes the cell behavior when kinetic limitations are reduced allowing thermodynamic behavior to be more fully explored. Using the unique cell signature from this cycle, incremental capacity analysis (dQ/dV) can be performed and high-fidelity dQ/dV peaks indicative of reactions in the cell can be resolved. Movement, height, and shape of each peak can be used to track and compare degradation pathways throughout testing. In the final cycle, HPPC is used to characterize the charge and discharge resistance of each cell across all states of charge. The HPPC procedure uses a 30-second discharge pulse followed by a 40-second rest and a 10-second charge. The discharge pulse is conducted at a 1C rate, and the charge is performed at a 0.75C rate. After the HPPC profile is completed, cells are discharged 10% of the minimum capacity at a C/3 rate. Each set of measurements is separated by a one-hour rest to allow the cell to equilibrate before another set of measurements is taken. During HPPC, the voltage should be limited to the cell upper voltage limit. In some cases, this may reduce the applied current before the 10-second duration is reached. When this occurs, the resulting resistance calculations should not be utilized due to the strong time dependence of battery resistance measurements. Similarly, incomplete discharge pulses near 0% SOC should not be utilized for comparison. Generally, 10 resistance calculations can be made from a single RPT, but this number will reduce with aging as the minimum voltage is reached more quickly.

Results

The cycle life test evaluates a cell's ability to deliver rated capacity while operating with moderate C-rate and ambient temperature (25°C) over long-term cycling. Cycle life testing provides a description of cell capacity, degradation, and stability over its useful life. Cells are cycled using a constant-current, constant-voltage (CC-CV) profile with a C/3 rate and CV current cut-off as detailed in the manufacturer's specifications sheet. Every 100 cycles, an RPT is performed to measure changes in battery behavior in relation to the baseline. If the cell reaches 70% remaining-useful-life (RUL) as based on the rated minimum capacity, cycling is stopped and a final RPT is performed. **Figure 3** shows an ongoing set of room temperature cycle life data from a batch of Li-ion 18650s. The average discharge capacity of the batch is plotted with standard deviation error bars versus cycle number. Each highlighted region indicates where an RPT was performed. In the **Figure 3** inset, an RPT is shown with each cycle's average capacity marked in black. The degree of variability when comparing cell capacities increases over time as clearly exhibited by the rise in standard deviation especially after 200 cycles. Each RPT can be used to elucidate changes in the cell resistance, capacity, and reaction profile as the cells follow different aging paths.

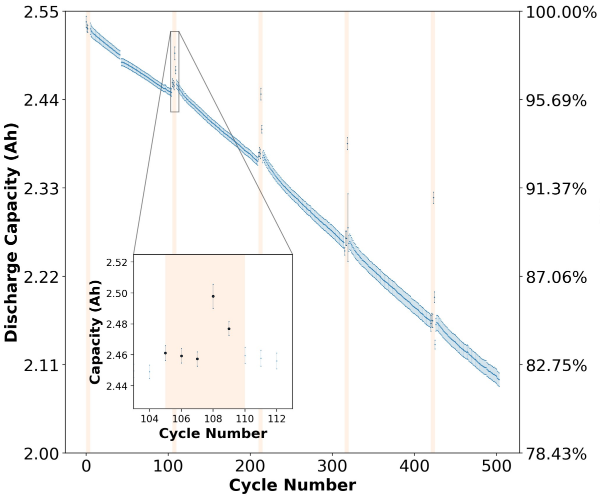

Figure 3. Cycle Life Data from a Batch of 5, Li-ion cells

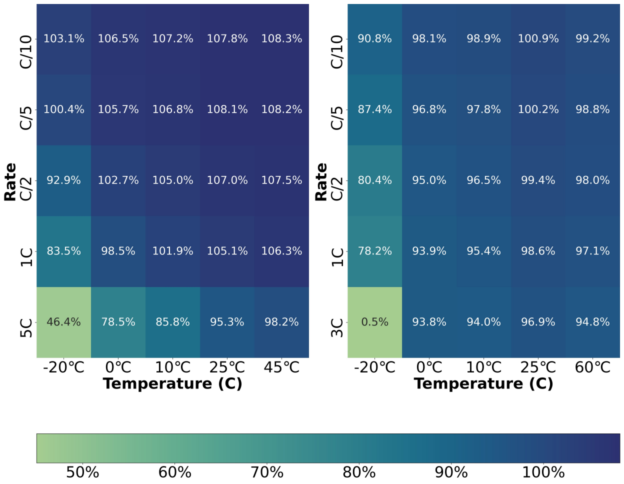

Figure 4. Percentage of Capacity Retention in terms or Rate Capability for a Na-ion pouch cell (left panel) and a Li-ion 18650 (right panel)

The rate capability test assesses current and capacity delivery over a range of temperatures. Cells are tested at 0°C, 10°C and 25°C as well as minimum and maximum temperature as listed on the manufacturer's specifications sheet. If a minimum or maximum temperature is not listed, -20°C and 40°C can be used instead. At each temperature, cells are tested at 5 rates: C/10, C/5, C/2, 1C and max C-rate. The resulting dataset can be visualized in a heatmap as shown in **Figure 4**. Testing cell-types over a range of temperatures and rates enables technologies to be matched with corresponding environments and rate requirements. Darker regions in the heatmap indicate a cycling condition that is favorable for the cell-type. Comparing the lower left region of each plot in **Figure 4** where high C-rate and low temperature coincide, the Na-ion cell (left) exhibits significantly enhanced capacity retention even when cycled under a higher C-rate condition than the Li-ion cell (right). However, the Li-ion cell is rated for cycling at higher temperatures and exhibits a relatively insignificant capacity loss at 60°C except for near max rates.

A third consideration when choosing a battery technology for a particular application is its ability to store over long periods of time without degradation. Shelf life is a critical factor in determining which energy storage device to deploy when use will be intermittent leaving the battery to sit without cycling for months or years. The calendar life test investigates aging phenomena when a cell is stored at ambient temperature (25°C) and 100% State-Of-Charge (SOC) for long periods of time (~6-12 months). After cells are baselined, they are set inside environmental chambers where the temperature remains at 25°C, +/- 2°C. At an interval of ~30 days, the cells are removed and an RPT is conducted. It is worth noting that the cells must be discharged prior to performing the standard RPT procedure. Additionally, afterwards the cells should be charged back to 100% SOC and placed into the environmental chamber again. As with other tests, the RPTs serve as a window into the degradation caused by aging. Additionally, comparisons can be made between cycle life data and calendar life data to de-couple the effect of periodic cycling versus calendar aging during the calendar life test. Completion of all three tests provides a full-spectrum view of the capabilities of each cell-type. Further application-specific testing can be conducted as necessary after the cells are characterized in the standard tests.

Conclusions

Battery testing is a complex, but necessary topic to improve the utilization of emerging battery technologies. Battery data is highly context specific and cannot be interpreted fully without a set of metadata related to the conditions during testing. Without standardizing the conditions surrounding battery experiments, the resulting data can become incomparable with other data leading to a waste in research efforts and funds. A testing framework was presented which attempts to improve upon past testing methodologies from well-known battery organizations by creating a detailed, step-by-step procedure for neutral characterization of dissimilar battery technologies. The use of these procedures can enhance and enable cross-operability of data generated at independent battery testing facilities. Further research is needed to continue the refinement of these methodologies and increasingly provide a more well-rounded approach to characterizing and comparing pre-commercial cells.

Acknowledgements

The authors thank the U.S. Naval Research Laboratory for funding through the Naval Innovative Science and Engineering (NISE) program.

References

1. Battery Test Manual for Baselining & Benchmarking Pre-commercial Cells, Revision 1, NRL/6170/MR--2022/8, September 2021
2. Federal Consortium For Advanced Batteries Battery Test Manual, Revision 1, INL/MIS-21-62073, August 2021
3. USABC Electric Vehicle Battery Test Procedures Manual, Revision 3.1, INL/EXT-15-34184, October 2020
4. J. Christophersen, Battery Test Manual For Electric Vehicles, Revision 3, INL/EXT-15-34184, June 2015