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A Practical Design of Reliability and Performance Test for Portable Lithium-ion Batteries

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***Abstract* - Lithium-ion batteries are increasingly used in industry as an energy storage system for applications ranging from portable electronics to high-energy electric vehicle systems. Their reliability and performance in the field can be affected by variations in environmental and loading conditions. Performance characterization testing provides health and performance features that can be used to assess a battery's performance and reliability under a variety of field environments and usage conditions. This paper presents and discusses the performance characterization tests for lithium-ion batteries in portable electronic applications. A case study is also presented where beginning, operational, and end-of-life characterization tests are performed.**

Index Terms - Lithium-ion; state of charge; performance testing; reliability

I. INTRODUCTION

Owing to their high-energy and power capabilities, lithium-ion (Li-ion) batteries are used in many different applications ranging from portable electronics to large-scale electronic systems such as satellites and vehicles [1]. Li-ion batteries are produced with different chemistries such as lithium cobalt oxide ($LiCoO_2$), lithium iron phosphate ($LiFePO_4$), lithium manganese oxide ($LiMn_2O_4$), lithium nickel manganese cobalt oxide (NMC), and lithium nickel cobalt aluminum (NCA) [2]. As used in many different applications, it is important to understand the environmental and physical conditions that the Li-ion battery experiences changes for each application [3][4].

In order to study the degradation process of Li-ion batteries, performance tests are carefully chosen and applied to the experimental study [7]. Three types of testing are combined to properly characterize the Li-ion batteries at the beginning of, throughout, and at the end of the experimental process. Knowledge of the application and its performance requirements will assist in formulating and applying performance tests at the beginning of life (BOL), during operational life (DOL), and at the end of life (EOL) of the battery [5][6]. Among all, BOL performance testing allows testers to gauge the initial condition of the battery and enables them to determine appropriate test conditions so that the data collected is accurate and reliable. Additionally, the baseline values of battery health indicators can be determined to enable health monitoring throughout the battery's useful life. DOL performance testing allows testers to acquire data on the degradation trends as aging occurs and then compare the data to the baseline performance acquired through BOL testing. EOL performance testing is incorporated toward the end of the battery's life and can include destructive testing since the battery has already reached the end of its life. Alternately, EOL testing can be used to assess potential secondary uses for the battery. There is also a need to assign assessment criteria for how to consider the EOL of a battery system, which in most cases falls between 70% and 80% of the remaining capacity.

The remainder of this paper is organized as follows: Section 2 includes recommended reliability and performance tests for lithium-ion batteries in portable electronic applications. Section 3 discusses an accelerated-aging case study on long-term storage of $LiCoO_2$ cells and the subsequent degradation captured by BOL, DOL, and EOL performance tests. Finally, Section 4 presents the conclusions from this study.

II. BOL, DOL AND EOL TESTS FOR PORTABLE ELECTRONIC APPLICATIONS

Portable electronic devices experience many different environments due to their portable nature. The most common abuse setting is the environment in which these devices are being used and stored. In order to fully understand the degradation of batteries in portable electronics, reliability tests must be carefully chosen to best exemplify their actual use in the real world and their overall behavior over time. Below are the recommended reliability and performance tests that need to be employed so that accurate representation of the parameter degradation, such as capacity, is established. The recommended tests for portable electronic applications are listed in Table 1.

TABLE I TESTS FOR PORTABLE ELECTRONICS APPLICATIONS AND THEIR INTENDED PURPOSES.

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Test Description	Test Types	Purpose
Rate capability	BOL, DOL, and EOL	Measure discharge capacity and the effect of discharge rate on capacity
Differential scanning calorimetry	BOL, DOL, and EOL	A thermo-analytical technique where the temperature difference of a sample and reference is measured as a function of temperature.
Impedance test	BOL, DOL, and EOL	Impedance spectroscopy can be used to measure changes in ohmic resistance, charge-transfer resistance, and diffusion.
Weight and dimension measurement	BOL, DOL, and EOL	Li-ion batteries can lose or gain weight as a result of exposure to humidity or the release of gas. Additionally, swelling of the cells can place mechanical constraints on portable devices.
Cycle life test	BOL, DOL, and EOL	Cycle life testing can be used to identify the number of cycles a battery can operate before crossing a performance threshold.
Calendar aging test	DOL	Performance loss is a result of active charge/discharge cycling, as well as inactive calendar aging. Calendar aging testing can be used to quantify performance loss while the battery is not in use.

III. Experimental Design at CALCE for Portable Electronic Battery Storage Reliability

In order to conduct an experiment that measures irreversible capacity loss during storage given a combination of SOC and temperature, characterization tests are employed on a batch of cells to check their relevance and applicability for the storage experiment. The following performance tests and results are derived from the initial BOL performance tests, and the exact same procedure for each test is employed for the lithium-ion cells after aging has occurred. For simplicity, preliminary results for BOL tests are provided given the fact that DOL and EOL tests follow the same procedure and methodology. It is important to note that the results will in fact be different but that the overall testing procedure is the same.

A. Procedure

The samples used were commercially available 1.5 Ah pouch lithium-ion cells with a lithium cobalt oxide ($LiCoO_2$) cathode and graphite anode. Performance characterization tests were conducted in order to check whether the chosen battery samples were applicable for long-term cycling operation. This characterization procedure includes BOL, DOL, and EOL performance tests that were developed to help evaluate the performance of the samples in question and verify the manufacturer's credibility. The methodology for the initial characterization derived in this particular study entails the following steps:

Firstly, all of the 25 samples are labeled, e.g., PL_1, PL_2 … PL_*n* (PL = pouch lithium, *n* = cell number). Then, physical measurements of each cell were taken including the height, width, length, and weight for each sample, which will be used as references to compare with aged cells later. X-ray analysis was also performed on all cells to examine the internal electrode structure, tab placement, and try to identify any manufacturing defects.

Once physical characterization is performed, the batteries can undergo electrical characterization. Using an Arbin BT2000 commercial battery tester (Fig.1), cells were charged and discharged using a constant current constant voltage (CCCV) profile at a rate of C/2 (750 mA) with an upper voltage limit of 4.2V and a lower voltage limit of 2.75V. The constant voltage step ends when the current falls below C/100 (15 mA). The cells were allowed to rest for 1 hour in between charge and discharge steps. At that time, DC internal resistance (DCIR) and electrochemical impedance spectroscopy (EIS) measurements were taken.

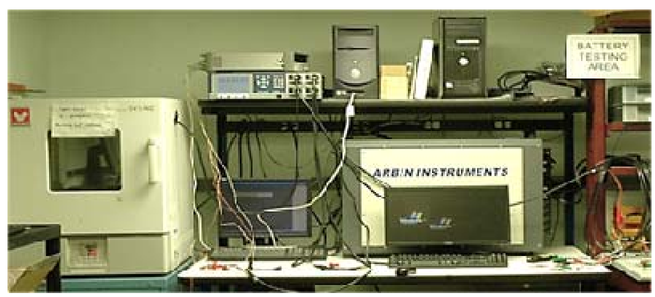

Fig 1. Arbin BT2000 commercial battery testing system.

Finally, when the Li-ion batteries went through a charge/discharge/charge profile, they were then subjected to a pulse-power (PP) characterization for each cell. The PP test verifies the pulse power being delivered during minimum and maximum charge.

B. BOL, DOL, and EOL Physical Characterization Tests

(a) Dimensions and Weight

In order to properly compare the initial performance characteristics with the future performance of $LiCoO_2$ cells, a detailed investigation at the cell-to-cell level must be performed and consequently observed. Variance in the weights and dimensions of the battery cells can provide the user with information on the quality control of the manufacturer. A large deviation of a cell from the averaged value of the whole lot may indicate that some manufacturing defects may exist for that cell. Therefore, when weights and dimensions are recorded, comparison to the manufacturer specification sheet can quickly determine whether certain cells could be defective. With a reduced volume or weight, the composition of the active material could be altered from the pre-specified manufacturer specification, thereby making it easier to identify and remove problematic cells.

An analytical balance scale is usually used to accurately measure the weights of the samples in a controlled environment. As shown in Fig. 2, the weight values of test samples are distributed uniformly, although there were some samples with significantly reduced weight. With such inspection, identification of the defective cells becomes a much easier process. In Fig. 3, the volumes range from 14,042 mm^3 to 14,685 mm^3, which is a large variety of cells that have different volumes. With such inspection, identification of the defective cells in terms of a lack of active material becomes much easier.

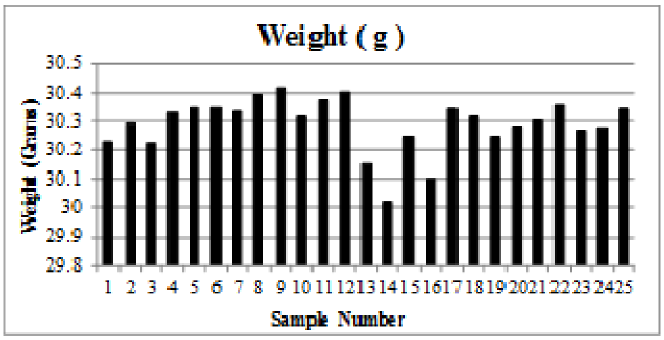

Fig 2. A histogram of the PL battery weights.

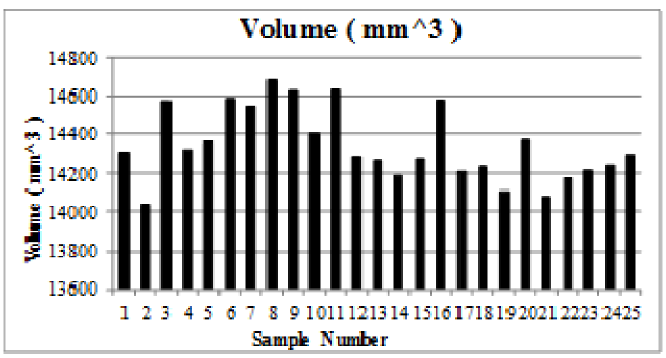

Fig 3. A histogram of the PL battery volumes.

(b) X-ray Analysis

X-ray analysis can be used to non-destructively investigate the internal structure of the cell. As a battery ages, structural changes can occur that accompany performance degradation. For example, the cause of failure via the delamination of the active materials from the current collectors that cause morphology changes will be visually discernible from the X-ray without destroying the cell.

According to [8], X-ray tomography methods are used to investigate lithiation-induced stresses that lead to delamination and microstructural changes. Results from the experiment showed that samples received from the manufacturer that had air voids were more prone to delamination. From the results it is evident that upon the volumetric expansion of the anode, the current collectors were subsequently affected by delamination and the creation of air voids within the cell. Such a degradation mechanism can impact the performance of the cell. Therefore, the use of X-rays can provide valuable information that can screen battery cells for defects before being used in full-scale testing. X-ray testing can be used to study battery cells at the cell level and to identify any visual differences. More importantly, a collection of the X-ray images during initial and future testing can allow a comparative study between the two and show how the morphology of the cell changes.

(c) Temperature Measurements

Lithium-ion battery performance and degradation is very sensitive to changes in the ambient temperature and heat generated within the battery. Temperature sensors, specifically thermo-couples, can be attached to individual cells to identify heat generation under different operating profiles. Furthermore, the ability to develop an accurate representation of the temperature variations that a battery cell experiences when under a charge/discharge profile can significantly aid in the determination of potential safety concerns as well as help mitigate certain side-reactions such as thermal runaway [9]. Each of these relationships between temperature and voltage is measured for the first charge, first discharge, and second charge. An accurate representation of the temperatures for each voltage and current allows the user to determine how temperature fluctuates when a battery is charged and discharged. Such information will be useful when trying to derive future data to develop trends that show how temperature fluctuations degrade the cell after it has been aged.

C. BOL, DOL, and EOL Electrical Characterization

(a) DC Resistance

DC resistance is a function of temperature, state of charge, and state of health [10]. Resistance measurements were recorded for each of the cells when fully charged (100% SOC) and fully discharged (0% SOC). Fig 4 shows that the samples did not have much variation in their internal resistance characteristics for each step of the charge/discharge/charge profile.

According to [8], resistance can be used as a parameter to evaluate the state of health of a battery cell. High resistance within the cell can cause a large ohmic loss when a battery is under load. This causes the battery's voltage to reach its lower limit more quickly, and as a result, the battery's usable capacity and power performance is diminished. As shown in Fig. 4, it is clear that all cells performed in a similar fashion, maintaining a resistance value between 0.1 • and 0.04 •. Interestingly, two particular cells had resistance values that were considered to be outliers. The outliers occurred after the second charge and could have been produced by a faulty connection or by a manufacturing defect in the $LiCoO_2$ battery cell.

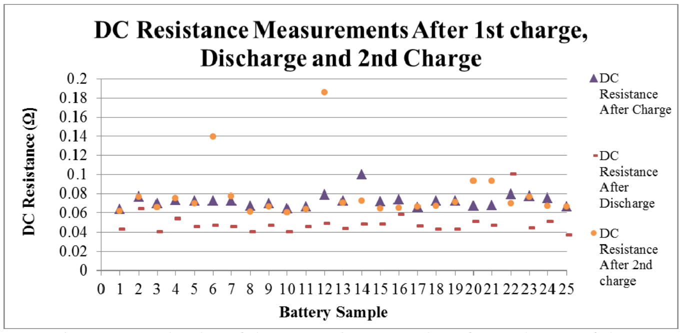

Fig 4. Example plot of the DC resistance values for each step of the charge/discharge/charge profile.

(b) Impedance Spectroscopy

AC impedance was measured using electrochemical impedance spectroscopy (EIS) between 0.01 Hz and 2 kHz. Measuring the battery's impedance at different stages of degradation can be used to determine the state of health of the battery. AC impedance provides more information than DC resistance about the diffusivity of cell, which is closely related to the power capability of the cell. According to [11], impedance results can help show how battery cells age and how the resulting performance diminishes. In this case study, impedance measurements were taken when the cell was fully charged (100% SOC) and fully discharged (0% SOC). Differences in the initial impedance of a battery can help identify cells that do not meet pre-defined performance thresholds.

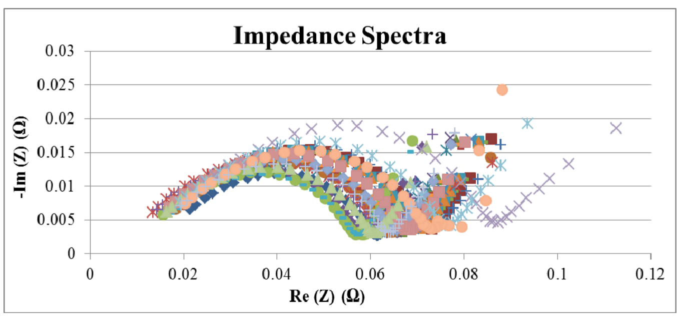

Fig 5. All 25 cells underwent an impedance test right after the first charge

Fig 5 shows the impedance measured after the first partial charge. At the beginning of the plot, the pure uncompensated Ohmic resistance (R.) varied minimally between the samples. To the right side of the semicircle, the uncompensated Ohmic resistance includes the charge-transfer resistance. The resistance range experienced by the cell is increased, and the imaginary part of the impedance—the reactance portion—slightly increases. The impedance plots of the cell samples for the full discharge do not vary as much, but rather seem to follow a similar trend, especially the leftmost point of the impedance plot.

Fig 6 provides the impedance results for after the last full charge. On the right of the impedance plot the Ohmic resistance and charge-transfer resistance vary between all the cells by 0.03 •. As shown in Fig 7, there is a maximum impedance value and a minimum impedance value for all of the cells. Comparing these two values, we can find the range of impedance and the variance for each component of the impedance plots (reactance and resistance). The range for the reactance portion of the impedance plot for low frequencies almost remains constant, although at higher frequencies the reactance range reaches a maximum at a middle frequency of 0.05 •. On the other hand, looking at the resistance portion, we can see that the range has a value of 0.025 •.

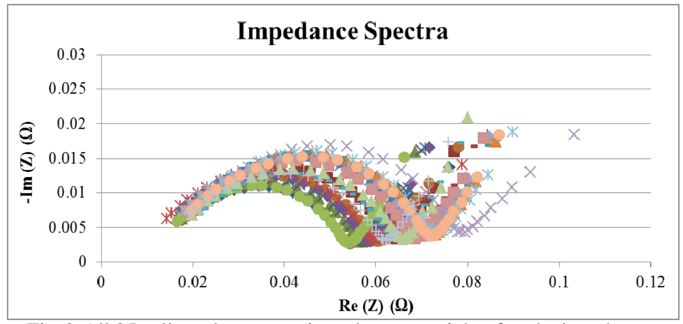

Fig 6. All 25 cells underwent an impedance test right after the last charge.

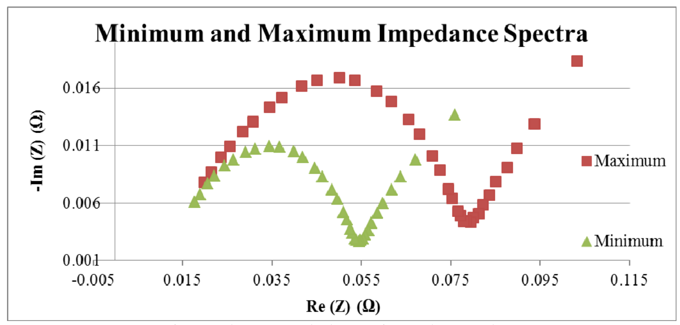

Fig 7. The second charge impedance plots.

When future testing is conducted and impedance values are recorded, the degradation trend of the battery cell in question can be developed, analyzed, and compared to the values found in the initial characterization. It is important to keep the impedance test consistent. The impedance changes as a function of state of charge as well, and impedance measurements taken at DOL and EOL should be at the same state of charge and temperature so that the results can be consistent and applicable for use in health monitoring.

(c) Open Circuit Voltage

Many battery models require a relationship between the open circuit voltage of the cell and the state of charge [12]. To find out the relationship between OCV and SOC, three samples were discharged with a 1-min discharge pulse at a C/10 rate (0.075 A), followed by a rest period lasting 30 min to allow the battery to reach thermal and chemical equilibrium. This profile was repeated until the battery was fully discharged. Fig 8 shows that the OCV varies almost linearly with SOC from the 100% value to the 10% value. However, below 10% the OCV drops significantly.

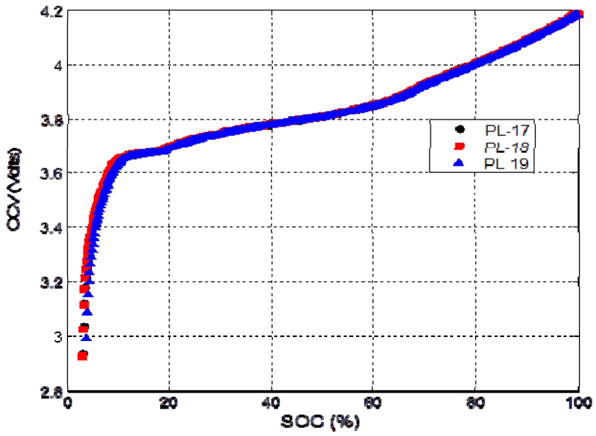

Fig 8. The open-circuit voltage (OCV) and state of charge (SOC) relationship during initial cycling.

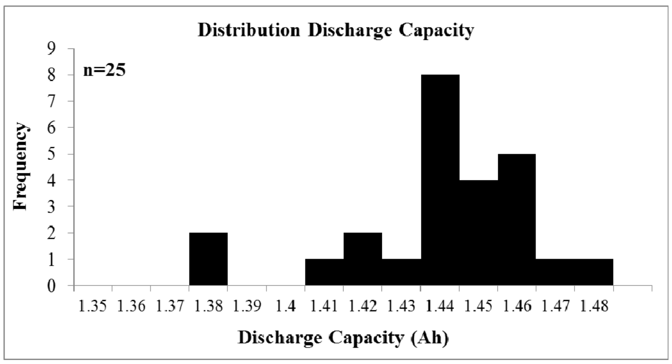

Fig 9. A discharge capacity distribution shows that the majority of cells were observed to have a discharge capacity above 1.44 Ah.

(d) Discharge Capacity Testing

During the initial testing for characterization, a discharge capacity profile was developed by using the data generated from the charge-discharge-charge profile (CDCp). By knowing the discharge capacity information, a good approximation can be developed that shows how the battery initially operates compared to the given specifications that the manufacturer claimed. The $LiCoO_2$ battery cells were rated at 1.5 Ah at a discharge rate of C/5 (0.15 A) on their specification sheet. Depending on the application, higher discharge rates may be necessary, and testing should be performed under realistic operating conditions to assess the cell's performance under life cycle operating conditions. Measuring the discharge capacity before the cells go through cycling can provide reference to quantify cell degradation, as well as indicate initial inconsistencies that might cause problems during future testing. Even at a discharge rate of 0.5C (0.75 A), the cells performed close to their rated capacity, although there were certain cells, such as PL20 and PL22 that experienced a reduced discharge capacity of about 1.3789 Ah. This loss in capacity accounted for about an 8.8% total reduction from the rated capacity. From visual inspection of the discharge capacity histogram (Fig.9), it is evident that not all battery cells performed according to specification with a rated capacity of 1.5 Ah.

IV. Conclusions

Lithium-ion batteries are becoming popular as an energy storage system for applications ranging from portable electronics to high-energy electric vehicle systems. Safe and reliable operation of lithium-ion batteries requires a proper methodology for testing. Performance tests are divided into three different testing groups: BOL, DOL, and EOL performance tests where the data quantify the degradation experienced by the cell. Among these three tests, BOL tests include, but are not limited to, dimension and weight measurement, X-ray, discharge capacity, and impedance/resistance tests. DOL tests include most BOL tests and are considered to be reference performance tests that would be used in comparison to aged states. To derive accurate and reliable results on performance, appropriate scaling needs to be implemented in order to optimize the test according to constraints that the chemistry and application-specific cell experiences. Performance tests for applications such as portable electronics focus more on capacity performance tests to measure the actual capacity delivered by the cell and pulse tests to derive relationships between voltage and SOC.

A case study on the irreversible capacity loss of Li-ion cells during storage using $LiCoO_2$ cathode cells for portable electronics is discussed with example performance tests and corresponding results. The results provide information on the performance of the Li-ion cells. Observations made for BOL, DOL, and EOL performance tests are also included, allowing the researcher to directly know what to look for when conducting future performance tests for new experiments.

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