Journal of Power Sources 280 (2015) 363–372

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Impact of high rate discharge on the aging of lithium nickel cobalt aluminum oxide batteries

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HIGHLIGHTS

- Three 3 Ah NCA batteries were discharged at different rates and conditions.
- One in a pulse manner, one at a high CC, and one at nominal 1C rate.
- Pulsed discharge had the highest impact on aging relative to other conditions.
- EIS modeling was performed to determine dominant mechanisms.

ARTICLE INFO

Article history:
Received 13 October 2014
Received in revised form
14 January 2015
Accepted 18 January 2015
Available online 21 January 2015

Keywords:
Lithium-ion batteries
Capacity fade
Impedance spectrum
Pulsed discharge
High C rate
Aging

ABSTRACT

In this study, three identical $LiNi_xCo_yAl_{1-x-y}O_2$, (NCA) batteries are evaluated to understand the impact of high rate discharge on the rate of capacity fade. The first of the three cells is repeatedly discharged in a pulse width modulated (PWM) manner at a frequency of 10 kHz, duty cycle of 50%, and peak rate of 83C (250 A). The second cell is repeatedly discharged at a constant current (CC) rate of 25C (75 A) while the third cell, which serves as the control cell, is discharged at its nominal CC rate of 1C (3 A). All three cells are recharged using a 1C CC recharge procedure to minimize the impact of recharge on cell aging. Novel and commercially procured battery cyclers are used to experimentally discharge and recharge the cells. Periodic baseline measurements, in which both capacity and electrochemical impedance spectroscopy (EIS) measurements show that the degradation mechanisms are enhanced under high rate pulse discharge cycling conditions. EIS modeling points to breakdown in the integrity of the anodic side double layer and increased charge transfer resistance as the largest contributors to impedance evolution in the cell.

1. Introduction

Over the past few decades, the world's dependence on batteries has risen to heights few could have imagined half a century ago. Advancements in battery technology have enabled new devices with extremely diverse capabilities, ranging from critical lifesaving devices all the way to entertainment systems In every one of these applications, degradation within the cells causes a gradual drop in their capacity to the point where they require replacement. The causes which contribute to battery aging have long been a topic of study, especially those which induce aging at nominal current ratings [1–6]. Many of these research efforts have shown that aging occurs in the bulk electrode and electrolyte materials, as well as at the interface between each respective electrode and the common electrolyte. At the anode/electrolyte interface, processes such as graphite exfoliation, electrode cracking, electrolyte decomposition, stabilization, expansion, dissolution, and conversion of the solid electrolyte interphase (SEI) layer, lithium plating, and corrosion are among the possible occurrences. On the cathode side, micro-cracking, electrolyte decomposition, gas evolution, conductive particle oxidation, dissolution, binder decomposition, surface layer formation, and oxidation are among the processes leading to capacity fade and power loss of the cell [1]. Broussely et al., previously

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http://dx.doi.org/10.1016/j.jpowsour.2015.01.110
0378-7753/

confirmed that energy loss results from the transformation of active materials into inactive phases and/or through increases in cell impedance; both of which lower the operating voltage of the cell and reduce its usable capacity. Similarly, they found that power capability loss is directly related to impedance growth and that most of the time both effects are jointly observed [3].

Historically, lithium-ion batteries have possessed high energy densities but only modest power densities. Recently, however, electrochemical cell manufacturers have produced high power cells with equivalent series impedances (ESRs) less than 1 mΩ, allowing for higher power cells. This reduced ESR has considerably increased the application space for which electrochemical energy storage devices can be used, including hybrid and all-electric vehicles [7–9] and electric-grid energy storage [10,11] among others. These new high power cells are capable of discharging extremely high rates, sourcing substantial current to their loads. Almost always, high frequency switch mode power electronics are used as a regulation device between the battery and the load. These voltage regulators extract current from the batteries in the form of high frequency pulses with varying duty cycle. The ability and need to source high currents at high pulsed rates causes one to ask how this type of repeated operation will impact the life of the batteries. Little to no documented research exists on how high power cells perform and age over time when they are discharged at rates well in excess of their 1C value (10–100 times C-rate) [12]. While little has been done investigating the aging when discharged in a continuous manner at high rates, even less has been done to investigate the aging that results from being discharged at high rate in a pulsed manner at high frequencies (10s of kHz). It is the aim of the work here to investigate these two scenarios.

Increased knowledge on degradation behavior in lithium ion cells under pulsed cycling conditions will be beneficial to many industrial applications. Pulsed charging and discharging conditions are quickly becoming more common in the energy storage industry. In wind turbine electrical generation systems, the rate of charge varies depending on the wind speed supplied to the turbine at any given moment. Therefore, the charging profile is constantly pulsing at different rates and time intervals [13]. Similarly, in hybrid electric vehicles (HEVs), the battery is pulsed discharged with random charge intervals in between. Manufacturers who design battery modules for HEVs are continuously striving to increase their lifetime in order to make these vehicles more practical. In order to properly design modules for these applications, the degradation characteristics of the cells need to be studied or modeled to determine which component or material can be altered to achieve the greatest gain in performance [14]. The most important aspect is determining what degradation mechanisms are dominant in a pulse power system compared to a continuous system. With a better understanding of these mechanisms, these applications could be refined and as a result change the face of the energy storage industry.

In this study, three identical $LiNi_xCo_yAl_{1-x-y}O_2$, (NCA) batteries have been experimentally evaluated to understand the impact of high rate discharge on the rate of capacity fade [15,16]. One cell has been discharged at a high pulsed rate, the second has been cycled at a high continuous rate equal to the average rate of the pulsed profile, and the final cell has been cycled at nominal continuous 1C rates to act as a control cell. The experimental setup used will be discussed and the results through 400 cycles on each cell will be presented as well.

2. Experimental setup

Two experimental cyclers are used in the work performed here. The control cell and the high rate constant current cell were cycled using a 4000 series battery cycler manufactured by Maccor Incorporated (Fig. 1A). The cycler provides five channels which can charge and discharge cells with potentials up to 5 V and at currents up to 240 A per channel. It has a measurement accuracy of ±125 mA and ±2 mV. On the other hand, the high rate pulsed discharge cell is cycled using a novel low impedance test stand designed and fabricated at UTA (Fig. 1B). This novel test stand has the capability to reach the desired current amplitudes and pulsed frequency rates which are desired for this study. The equivalent circuit model of the entire test stand is critical in differentiating the aging characteristics in the cycled cell. Therefore and equivalent circuit model (Fig. 2) is used to describe the entire resistive network which remains constant throughout the experiment. The design and construction of the stand, in both the discharge and recharge configurations, has been previously documented [17–20].

The impact of high rate pulsed discharge on the aging characteristics of a cell is dependent on its nominal properties. The datasheet properties of the tested NCA cell here are shown in Table 1. Additionally, the temperature of the cell is monitored by 3 T-type thermocouples to prevent any thermal events that may arise during the experiment (Fig. 3). The experimental procedure performed on each of the three respective cells being presented here is detailed in Table 2. The objective of the first of the three cells was to study, independently, the impact of high pulsed rate discharge on its cyclic aging. To achieve this, the cell was discharged at high pulsed rates, but recharged using a nominal 1C, constant current (CC) – constant voltage (CV) procedure. The novel test stand is used to discharge the cell at a peak C rate of roughly 83C. Because the test stand is unable to vary its resistance as the cell is discharged, the discharge rate also decreases proportional to the cell's voltage. The discharge frequency is 10 kHz with a 50% duty cycle. The second of the three cells was cycled at a continuous elevated discharge rate, equal to the average C rate recorded in the high rate pulsed discharge experiment, in attempt to discern the impact which the pulsed nature of the discharge has from the average high C rate itself. That particular cell was discharged using a 25C CC procedure and recharged using a 1C CC – CV procedure. Finally, the third cell is a control which was both charged and discharged using a 1C, CC – CV procedure.

As part of the experimental process periodic 1C baseline procedures, as laid out in Fig. 4, were performed to measure the capacity fade of each respective cell as a function of cycle number. The 1C charge/discharge procedure was used to ensure each of the three cells was being compared using a fair metric as cycling progressed. As part of the baseline procedure, electrochemical impedance spectroscopy (EIS) measurements were collected to assist in the characterization of the degradation mechanisms within the cell as they aged. EIS measurements were performed once each cell rested for at least 1 h after a respective charge or discharge procedure, providing sufficient time for the cell's diffusion process to reach its near steady state. A Metrohm potentiostat was used to apply a sinusoidal signal with amplitude of 10 mV over a frequency range of 20 kHz to 10 mHz. The cell's impedance measured during the applied signals provides the useful EIS data.

3. Results

3.1. High rate pulsed discharge experiments

Pulsed discharge experiments are conducted on the custom cycling rig described above. As previously mentioned, the discharge rate varies on the incident voltage of the cell since the rig's resistance cannot be varied. Figs. 5 and 6 show the voltage and current profiles recorded during the 3rd and 400th elevated pulsed discharge cycles, respectively. These plots show that it takes