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Cycle life testing and modeling of graphite/$LiCoO_2$ cells under different state of charge ranges

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HIGHLIGHTS

- A long-term cycle life study on graphite/$LiCoO_2$ pouch cells.
- Influence of SOC range and C-rate on cell capacity is investigated.
- Capacity loss is found to be affected by mean SOC, ΔSOC and C-rate.
- A power law model for capacity loss is developed using testing results.

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ABSTRACT

Lithium-ion batteries are used for energy storage in a wide array of applications, and do not always undergo full charge and discharge cycling. This study quantifies the effect of partial charge-discharge cycling on Li-ion battery capacity loss by means of cycling tests conducted on graphite/$LiCoO_2$ pouch cells under different state of charge (SOC) ranges and discharge currents. The results are used to develop a model of capacity fade for batteries under full or partial cycling conditions. This study demonstrates that all of the variables studied including mean SOC, change in SOC (ΔSOC) and discharge rate have a significant impact on capacity loss rate during the cycling operation. This study is useful in identifying the SOC ranges with slow degradation rates.

1. Introduction

Lithium-ion (Li-ion) batteries are a popular type of rechargeable battery due to their high specific energy and voltage, low maintenance, and absence of memory effect. However, like other battery chemistries, Li-ion batteries undergo aging. That is, there is an irreversible capacity loss due to various physical and chemical changes that depend on the life cycle environmental and use conditions of the battery [1,2]. The capacity loss limits the lifetime of batteries and may prevent their reliable operation in the designated applications. Under certain operating and abusive conditions, the failure mechanisms of batteries can result in catastrophic failure and safety issues as well.

The cycling operation reduces the capacity of a battery through a variety of concurrent failure mechanisms. Charge-discharge cycling of a battery puts mechanical stresses on the electrodes, causing particle fracture, reducing electrode porosity, and loss of active material connectivity [1,3,4]. Combined with electrochemical side-reactions between the electrodes and electrolyte such as formation and thickening of solid electrolyte interphase (SEI) layer, the cell gradually loses its energy storage capabilities [1–3]. In most practical applications, batteries undergo charge-discharge cycling only for partial SOC ranges as opposed to the full SOC (0%–100%) range. Hence, it is important to study the effects of partial SOC range cycling on battery life.

In the past, various studies have been conducted to investigate the effects of SOC and change in SOC (ΔSOC) on the cycle life of Li-ion batteries. These studies have been conducted for different cathode materials and different operating conditions. Bloom et al. [5] conducted an accelerated cycle life study on graphite/$LiNi_{0.8}Co_{0.2}O_2$ cells under two SOCs (60% and 80%) and two ΔSOCs (3% and 6%). At 25 °C they observed that cycle life, defined as time to 20%

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power loss, decreased with increased ΔSOC. However, they surprisingly found a significant improvement in cycle life on increasing the SOC from 60% to 80% and concluded that further testing would be necessary to elaborate on these results. Also the ΔSOC used in their testing was small enough to understand its effects on cycle life. In another cycle life study limited to 500 cycles on graphite/$LiCoO_2$ cells by Choi and Lim [6], they concluded that high charge cut-off voltages and a long float-charge period at 4.2 V or above had the most severe effects on cycle life. However, they found that the depth of discharge (DOD or ΔSOC) did not affect the cycle life. Hall et al. [7] conducted a life qualification study on lithium-ion cells for geosynchronous satellites and concluded that operational capacity loss linearly depended on DOD (ΔSOC). However, they did not observe any decisive effect of end-of-charge voltage (EoCV) on life in the examined EoCV range (4.1 V, 4.0 V and 3.9 V).

Ning and Popov [8] developed a first-principle model based on experimental data obtained for a mesocarbon microbead (MCMB)/Li_xCoO_2 pouch cell. Based on the simulation of this model under two EoCVs (4.2 V and 4.0 V) and two DODs (40% and 60%), they concluded that increasing the EoCV or DOD (ΔSOC) increased the capacity loss. Wang et al. [9] studied the cycle life of graphite/$LiFePO_4$ cells under five DODs (90%, 80%, 50%, 20% and 10%), six temperatures and four discharge rates and found a power law relation between capacity fade and charge throughput. They defined the charge throughput as the amount of charge delivered by the battery during cycling. Their results showed that the capacity loss was strongly affected by time and temperature, while the effect of DOD (ΔSOC) was less important at C/2 discharge rate. Belt et al. [10] conducted a cycle life study on carbon/physically-blended Li–Ni–Mn–Co layered-oxide and Li–Mn–O spinel cathode cells. They found that under charge-sustaining cycle profile [11] rate of capacity fade increased with increasing SOC.

Hoke et al. [12] used their charge power profile optimization [13] for lithium-ion batteries in electric vehicles to minimize the time spent by batteries at high SOC. A significant lifetime increase of nearly 4 years was observed in simulation when the batteries spent a majority of their operating time between 20% and 40% SOC as compared to between 70% and 90% SOC during a typical weekly driving profile. Lam and Bauer [14] cycled $LiFePO_4$ cells to study the effects of SOC, ΔSOC, temperature and discharge rates on capacity fade rate. They concluded that the both average SOC and SOC deviation from the average SOC affect the capacity fading rate. They also modified the Millner's crack propagation theory based model [15] relating average SOC and SOC deviation to capacity fade, since it deviated up to 30% from their measurements.

Watanabe et al. [16] cycled the cylindrical graphite/$LiAl_{0.10}Ni_{0.76}Co_{0.14}O_2$(NCA) lithium-ion cells in two different voltage ranges of 2.5–4.2 V (0%–100% SOC) and 3.48–4.05 V (30%–90% SOC) and found that batteries with a reduced voltage range, and thus SOC range, exhibited significantly slower capacity loss rate. Ecker et al. [17] conducted an accelerated study on carbon/$Li(NiMnCo)O_2$ cells to analyze the influence of cycle depth and mean SOC on cycle aging. They observed that rate of aging increased with increasing cycle depth (ΔSOC) almost linearly. Also they found that for a given cycle depth, minimum aging occurred in cells cycled around 50% mean SOC. However, the generalization of these results to other cathode materials and cell technologies requires more investigation. Wang et al. [18] investigated the influence of DOD (ΔSOC), temperature and discharge rate on the cycle life of graphite/$LiNi_{1/3}Co_{1/3}Mn_{1/3} + LiMn_2O_4$ cells. They found that although capacity loss increased at higher DODs, temperature and discharge rate had more significant impacts on capacity fade. Also they observed a linear relation between capacity loss and charge throughput as opposed to power relation found in Ref. [9].

It is clear from the literature review that there exist a lot of dissimilarities in the results, conclusions and the models regarding the effects of mean SOC and ΔSOC on the degradation of lithium-ion battery. Also even though graphite/$LiCoO_2$ is a widely used Li-ion chemistry, there is no extensive and long-term study available investigating the effects of SOC ranges (mean SOC as well ΔSOC) on $LiCoO_2$ cell capacity loss. This paper presents an experimental study aimed at quantifying the effects of mean SOC, ΔSOC and discharge rate on graphite/$LiCoO_2$ battery capacity. Also, the experimental results have been used to develop a capacity fade model. This study is useful in identifying the SOC ranges with slow degradation rates. These ranges can be used in real-life applications to minimize battery degradation.

The remainder of the paper is organized as follows: Section 2 outlines the experimental test procedure for performing the initial characterization and the cycling study. Section 3 discusses the capacity results from the experiments. Section 4 presents a capacity fade model followed by Section 5 which provides the conclusions from this work and identifies limitations of current work and possible areas for future study.

2. Experimental test procedure

Commercial graphite/$LiCoO_2$ pouch cells with a nominal capacity of 1.5 Ah (at C/5 rate) and a nominal voltage of 3.7 V were used in the study. An end-of-charge voltage of 4.2 V and an end-of-discharge voltage of 2.75 V were specified by the manufacturer. The charging and discharging of the cells were carried out using an Arbin BT2000 Battery Tester with 16 independent channels. All the tests were conducted in a semi-temperature controlled room with temperature of 25±2 °C.

As Li-ion batteries are used as electrical energy storage systems, various electrical parameters and characteristics are associated with them. These parameters and characteristics were determined initially to define standards for a comparison analysis later in this study. The determination of these parameters and characteristics also helped in checking the performance of the cells compared to the manufacturer specification sheet. The initial characterization tests for the cells included constant current constant voltage (CCCV) charge - constant current (CC) full discharge (4.2V-2.7 V) at C/2 rate to determine battery discharge capacity.

2.1. Test matrix

Different SOC ranges with different mean SOC and ΔSOC values were selected between 0% and 100% to understand the battery degradation behavior in different regions of full SOC range. The primary objective of this study is to find the effects of SOC ranges on battery cycle performance at a constant discharge rate of C/2. However, for the SOC ranges with mean SOC of 50%, the tests were conducted at two different discharge rates of C/2 and 2C. The purpose behind using two different discharge rates is to find if the relative performance of cells cycled under different SOC ranges gets affected from discharge rate. For 1.5 Ah cells used in this study, C/2 and 2C rates refer to 0.75 A and 3 A, respectively. Five SOC ranges were selected while keeping in mind the requirement of having enough data points to find the capacity loss model constants. Table 1 provides the number of cells that were tested under each of the mean SOCs, ΔSOCs and discharge C-rates.

2.2. SOC estimation

The conventional Coulomb counting method was used to estimate the SOC of test cells during cycling. The SOC estimation was done using following equation: