Cycle aging studies of lithium nickel manganese cobalt oxide-based batteries using electrochemical impedance spectroscopy

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ABSTRACT

The cycle aging of a commercial 18650 lithium-ion battery with graphite anode and lithium nickel manganese cobalt (NMC) oxide-based cathode at defined operating conditions is studied by regular electrochemical characterization, electrochemical impedance spectroscopy (EIS) and post-mortem analysis. The study finds that capacity fade, impedance rise and the end-of-life of cycled cells strongly depend on the operating conditions like temperature, current rate, depth-of-discharge and mean state-of-charge. In general, the capacity fade is characterized by a slow linear decrease at first, followed by a rapid decrease. This transition point is found to correlate well to the rate of solid electrolyte interphase (SEI) resistance growth at the anode. A longer lifetime is found for cells cycled at 45 °C than at 20 °C for the same depth-of-discharge and C-rate. Effect of cycle depth on capacity fade is related to the graphite electrode volume changes and the local electrochemical potential at the electrodes. Cells cycling upto 4.2 V are found to have longer linear capacity fade but a higher total resistance. A more stable SEI at the anode and greater surface modifications on the cathode are inferred to be the reasons for this non-intuitive behaviour.

1. Introduction

The use of lithium-ion batteries in the fields of consumer electronics, transportation and energy storage is a growing market. Their high volumetric and gravimetric energy density compared to other battery chemistries makes them suitable for many applications providing multiple advantages. For example, deploying energy storage systems in electrical grids can have simultaneously economical benefits for the grid operator and lead to cost reduction for the consumer. In the transport sector, electric vehicles not only provide better performance but also help in meeting the emission targets. Unfortunately, the costs of lithium-ion batteries are still a hindrance to their fast adoption. Greater understanding of battery degradation processes and lifetime can be one way to bring down these costs.

Aging of lithium-ion batteries is measured by capacity fade and power fade. They have been studied by many groups [1–8].

Commonly, aging of lithium-ion batteries is divided into calendar and cycle aging [1–8]. Calendar aging is influenced by the storage parameters, namely the temperature and the state of charge (SOC). The degradation during cycle aging depends on the operating parameters: temperature, state of charge (SOC), current amplitude and depth of discharge (DOD). For both, calendar and cycle aging, aging mechanisms are usually investigated by alternating electrochemical characterizations at a reference condition with storage or cycling periods at predefined conditions.

Temperature affects cycle aging mainly because of the Arrhenius dependence of desirable and undesirable reactions on temperature. It has been found that higher temperature leads to greater capacity fade [4,9] in NMC cathode - graphite anode batteries. Leng et al. [10] found that degradation mechanism in graphite is enhanced at high temperatures. Instead An et al. [11] suggest a more stable SEI at high temperature. Schuster et al. [12] even found a lower capacity fade at 50 °C than at 25 °C, with an optimum at 35 °C for a NMC-graphite battery.

The dependence of capacity fade on DOD and SOC is studied due to its importance in deciding the usable capacity of the battery as well as the operating strategy. For batteries with NMC cathode and

graphite anode, Schuster et al. [12] found that at higher DOD, a higher capacity fade is seen. Higher DOD means that the cell reaches high and low SOC states, leading to more SEI formation and greater active material loss in graphite, respectively. Similar results were found by Wang et al. [5] but in their case at higher rates this dependence was not clear. Schmalstieg et al. [13] discovered that mean SOC around which the cell is cycled is important to understand DOD dependence. Capacity fade for 10% DOD was found to be fastest at high and low SOC and lowest at 50%. Ecker et al. [14] found that at 50% SOC, the deeper the cycle (greater DOD), the higher the capacity fade.

Studying cyclic aging dependence on current rate is especially relevant for high power applications such as fast charging. Higher rates were found to lead to faster degradation due to more stress in cells [5,15,16]. But Wang et al. [5] discovered that with increasing temperature, the dependence of capacity fade on current rate decreases. Schuster et al. [12] found out that more capacity fade is caused at higher charge rates which they attributed to lithium plating. While at higher discharge rates, less capacity fade was seen. An et al. [11] discovered that the SEI formed at higher current densities has a higher porosity and electronic conductivity, which are undesirable properties for SEI.

Spotnitz [1] identified 4 different stages of capacity fade during cycle life, with the first three stages often indistinct and slow and the last one conspicuously steep. This rapid decline in capacity loss is well documented in batteries [1,3,12,14,17—19].

In this study, cycle aging of a commercial NMC-graphite cell has been quantified by electrochemical characterization. Studies on calendar aging on the same battery have been published before [20]. Cyclic aging has been studied for the parameters, temperature (0 °C, 20 °C, 45 °C), current rate (1 C charge − 1 C discharge (C1D1), 1 C charge − 2 C discharge (C1D2)), DOD (25%—100%) and mean SOC (25%, 50%, 100%). New insights into the cycle aging behaviour of the cells as a function of the studied parameters result from statistical data analysis of the non-destructive characterizations including capacity determination, pulse tests and electrochemical impedance spectroscopy. Detailed investigation into the rapid capacity fade phenomena has been conducted. Its importance in end-of-life determination has been emphasized. Post-mortem analysis has been conducted at different stages of aging to investigate further the degradation processes in the electrodes. The concept of critical SEI resistance has been suggested as a possible metric for battery operation regulation. Degradation parameters for this battery have been quantified and presented in this work.

2. Experimental part

2.1. Tested batteries

In this study high energy cylindrical cells of the type US18650V3 manufactured by Sony Energy Devices Corporation were tested. The cell has a lithium nickel manganese cobalt oxide (NMC) cathode and a graphite anode with a rated capacity of 2.15 Ah determined at a discharge current rate of 0.2 C. The rated capacity is used as reference for calculating current rates (C-rates). The upper and lower voltage bounds are 4.2 V and 2.5 V, respectively. Electrochemical characterization and cycling of the cells were done with same equipment as described in Schmitt et al. [20].

2.2. Characterization

The electrochemical characterizations of the cells were carried at their thermodynamical equilibrium at 20 °C. The steps of these characterizations are already described in Schmitt et al. [20]. Here, just the definitions as used in this article are reiterated. The actual

Table 1
Test matrix of studied cycle conditions around the mean SOC in %. The parameter CxDy represents (C)harge and (D)ischarge with current rate x and y, respectively.

DOD/%	CxDy					
	$T = 0\,°C$		$T = 20\,°C$		$T = 45\,°C$	
	C1D1	C1D2	C1D1	C1D2	C1D1	C1D2
25			50	50		
50	50	50	25/50/75	50	50	50
60/80/90			50			
75			50	50		
100	50	50	50	50	50	50

cell capacity $C_{0.1C}$ is analysed which was determined during the discharging phase with a current at $C_{0.1C}$. Thereafter, electrochemical impedance spectroscopy measurements were conducted on the cells at a SOC of 50%. The frequency range was between 2 kHz and 10 mHz. The measurements were conducted in galvanostatic mode with the ideal voltage response as 10 mV. Eight measurements per decade were taken and the maximum AC amplitude was set to 0.2 A.

2.3. Cycle aging tests

The combinations of tested temperatures, DOD, charge and discharge currents CxDy and mean SOC for cycling are shown in Table 1. If the operating conditions of a cell are DOD = 50% with a (mean) SOC = 75%, the cell is cycled between 50% and 100% SOC. To ensure repeatability, each test was performed with three cells. Because of the high repeatability of the data, an average of the three cells is presented in this work (unless otherwise mentioned). After each characterization the charge and discharge capacity has to be adapted from the DOD, since the actual cell capacity C_{1C} reduces with aging. The sequence of one cycle for each cell was the following: (i) CCCV charging by 1 C until the current had decreased to 0.05 C, (ii) pause of 30 min, (iii) CC discharging of a certain DOD at defined current rate, and then (iv) pause of 5 min. Note, that the occurrence of the CV charging phase in step (i) depends on the DOD and the aging of the cell.

The cells were cycled at defined conditions until the total (charge and discharge) capacity reaches 100 equivalent full cycles (EFC), where one EFC is defined as the ratio of the capacity normalized to twice the nominal capacity, i.e. charging and discharging at DOD 100% gives one EFC. Some cycle test needed to be stopped before 100 EFC due to technical issues. After cycling, if required, the cells were placed in a 20 °C temperature chamber.

Additional aging tests for studying cross correlation between the two parameters, temperature and DOD, are tabulated in Table 2. The cells were first operated at the operating conditions (T_1, DOD_1) for 200 EFC and then switched to (T_2, DOD_2). The cell testing for these cells also began about two years later than the other cells.

2.4. Other cell tests

Electrode materials both graphite and NMC were also recovered

Table 2
Test matrix for correlation studies with charge and discharge currents of C1D1 and 50% mean SOC. The arrow indicates the change to different operating conditions.

$T_1/°C$	$DOD_1/\%$		$T_2/°C$	$DOD_2/\%$
20	50	⇒	45	50
45	50	⇒	20	50
20	50	⇒	20	100
20	100	⇒	20	50