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Introductory Invited Paper

Increasing the cycle life of lithium ion cells by partial state of charge cycling

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ABSTRACT

In this study, the possibilities to enhance the cycle life of Li-ion cells were explored. Cells were charge-cycled in different ways. Discharging from the fully charged state down to several levels showed that the cycle life is determined by the total amount of transferred charge. Cycling a fixed amount of charge from a partially charged state leads to longer cycle life as the initial state of charge is lower. Impedance spectroscopy showed that the solid electrolyte interface forms the main contribution to the degradation of the cells.

1. Introduction

Although rechargeable batteries are very reliable — the failure rate is in the range of 5–500 failures per one billion operating hours [1] — their lifetime is quite often the critical factor in many applications. It is thus justifiable to investigate the factors that determine the batteries' lifetime, to develop predictive models, and to explore methods to extend the lifetime.

It is known that the cycle life of batteries can be prolonged by cycling less charge. This was observed in various depth-of-discharge experiments [2–4]. The straightforward explanation is that upon charging and discharging charge carriers are transported into and out of the electrodes, which leads to damage that accumulates with each cycle. Also lithium-plating adds to the reduced capacity of the battery [5,6]. Quite often tests are done by discharging a completely charged cell to a certain level, and charging again to the maximum level. In the second place, also partial charging to a lower maximum voltage increases the cycle life for the same reason of transporting less Li. A logical sequel is then to investigate the cycle life of partially charged cells.

Not much has been published on this subject, in particular not as far as Li-ion batteries are concerned. One study involved predicting the expected use of a battery for a certain period, and optimizing the charge for each particular of such situations [7]. The cycle life could be increased by up to a factor of 2.5, depending on the scenario. In another work Li-ion cells were subjected to small capacity excursions of $\pm$3–6% at SoC-levels of 40–60% [8]. The 3%-capacity cycle led to much longer cycle life. Similar was done by cycling $\pm$5% around the state of charge at different SoC-levels [9]. At a SoC-level of 50% the degradation was smallest as compared to SoC-levels of 25% and 75%. Only one investigation concerned Li-ion cells by cycling a larger amount of 25% of the nominal capacity around various SoC-levels [10]. That work puts emphasis on the estimation of acceleration factors for the cycle life. Further investigations addressed lead-acid batteries. In a study to batteries operating in remote power supply systems, it was claimed that a threefold increase of the batteries' lifetime can be gained [11]. Improvement of the performance by reducing unwanted side effects is possible by this method, as described in a general expose [12].

In this work such so-called partial state-of-charge (PSoC) cycling tests are described which were done on $LiCoO_2$-(NCR) cells of Sanyo. A large amount of capacity of 60% of the total nominal capacity was cycled at three SoC-levels.

2. Experimental

2.1. Test equipment and materials

Batteries of following model were tested: NCR18650F, $LiCoO_2$-electrode, with 2900 mAh capacity. For the cyclic charging and discharging Maccor and BaSyTec test machines are used. The Maccor-4300 has eight channels and the Maccor-4000 and the BaSyTec have 32 channels. Electrochemical impedance spectroscopy is done with an eight-channel Maccor EDA-0305 frequency response analyzer. This equipment can be connected to the cycle testers. All tests were done in an air-conditioned laboratory at 25 °C.

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2.2. Partial SoC-cycling

As explained in the Introduction, either discharging to a lower depth of discharge or charging to a lower maximum voltage leads to a longer cycle life. Therefore, special experiments were designed to charge and discharge batteries with a fraction of the total capacity, and to do such from various states of charge. In Fig. 1 the basic principle is illustrated. From a certain state of charge an amount of charge (ΔQ) is extracted from the cell and the cell is recharged again. This is done for various SoC-levels. Fig. 2 shows a typical discharge curve recorded for $LiCoO_2$-(NCR) cells.

For these experiments ΔQ = 60% of the maximum capacity was taken. To monitor the state of health, at regular intervals a standard cycle was taken with a full charge and discharge. The test scheme is shown in Table 1. Thus, NCR-batteries were discharged with 60% capacity from various state-of-charge levels represented by the respective maximum voltages. One test was done by discharging 60% from such voltage to reach the cut-off voltage of exactly 2.5 V (see rightmost case of Fig. 1).

The Li-ion cells are charged in two subsequent stages: constant current (CC) followed by a constant voltage (CV) step. These two subsequent charging steps are denoted by CCCV. During the CC phase, the charger applies a constant current to the battery at a steadily increasing voltage until the maximum voltage limit Vmax of the cell is reached. During the CV phase, the charger applies a voltage equal to the maximum cell voltage Vmax to the battery, as the current gradually declines towards zero, until the current is below a cut-off threshold. A typical value for the cut-off current is 5% of the initial constant charge current. For the situation where the cells are discharged from SoC = 60%, only the constant charge mode was employed.

In Fig. 3 a part of a test sequence is shown for clarity. The figure contains a number of monitoring cycles with the PSoC-cycles in between. As definition for the end of life, the number of monitoring cycles to reach 80% of the initial cell capacity was taken.

One remark must be added at this point. The capacity of the cells gradually degrades because of the continuous charge cycling. Therefore, the notion "state of charge" is not unambiguous since it relates to the actual capacity. Still, for clarity, we will use the SoC as a percentage of the initial capacity (see Table 1) to identify the different experiments.

2.3. Supporting cycling experiments

Apart from the PSoC-cycling tests, a number of supporting experiments were done. In one series fully charged cells were discharged to various levels. The depth of discharge was 100, 75, 50, and 25%. The state of health was monitored by a full charge–discharge cycle every 50 cycles. The other experiments were done by complete discharge of cells from various SoC-levels. These were 100, 90, and 80%. Here, only after the test such monitoring cycles were done.

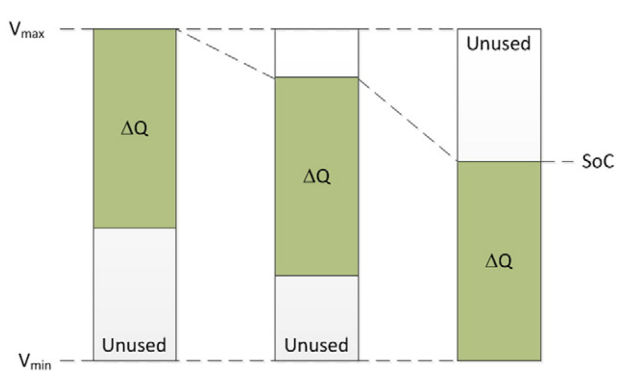

Fig. 1. Principle of partial discharge (ΔQ) from various states of charge (SoC).

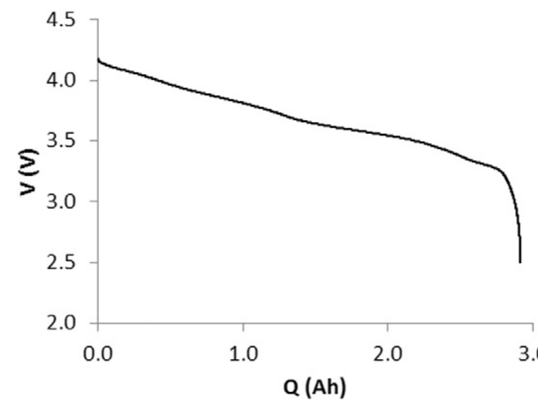

Fig. 2. Typical discharge curve for NCR-cell.

Finally, cells were continuously cycled to 100% DoD for 900 cycles. After each 50th cycle an impedance spectrum was recorded. This method is introduced in the next paragraphs.

All of these tests were done at 25 °C with a current of C/2 (charge) and 1C (discharge).

2.4. Impedance spectroscopy

A rechargeable battery is usually treated as an electrochemical cell [13]. Measuring the impedance as a function of the frequency gives detailed information on the various transport processes that take place in the cell, and in particular on the changes that occur during aging.

In Fig. 4 the schematic of a Li-ion battery is shown together with the solid electrolyte interface layer that grows during charging and discharging. The electrical conduction in such a system undergoes sudden changes at an interface, which leads to piling up of charge and a space charge is formed. It takes time for the charge carriers to be distributed again and reach a state of equilibrium. The type and nature of the interfaces determine the rate of these transport processes.

In order to further investigate the system and its various transport processes, a replacement scheme is needed in terms of basic components. There is no unique scheme, but in the upper part of Fig. 5 a very common representation of a rechargeable cell is shown. If implemented in a computational routine, it can be used to analyze the measured spectra. The elements describe the following processes:

- Series bulk impedance of the cell (current collectors, electrolyte, separator): L_s, R_s
- Migration of Li^+-ions through surface film layers (e.g. SEI): C_{SEI}, R_{SEI}
- Charge transfer resistance between electrolyte and electrode: R_{ct}
- Double layer capacitance between electrolyte and electrode: C_{dl}
- Diffusion of Li^+-ions between active material and electrolyte: CPE_{dif}.

Table 1
Test scheme of PSoC tests for NCR-cells. The upper block shows the settings for the long-life cycles with partially charged cells from various SoC (ΔQ = 60%). The lower block shows the settings for the standard cycles to monitor the SoH (ΔQ = 100%).

	Parameter	SoC unit	100%	75%	60%
PSoC-cycle	V max	V	4.20	3.90	3.76
	V min	V	3.64	3.42	2.50
	I-charge	C-rate	C/4		
	I-discharge	C-rate	C/2		
	Procedure	–	CCCV	CCCV	CC
	ΔQ (60%)	Ah		1.70	
Standard cycle	V max	V		4.20	
	V min	V		2.50	
	I-charge	C-rate		C/4	
	I-discharge	C-rate		C/2	
	Procedure	–		CCCV	
	ΔQ (100%)	Ah		2.75	