Journal of Power Sources 239 (2013) 45–53

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

Influence of relaxation time on the lifetime of commercial lithium-ion cells

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HIGHLIGHTS

- A relaxation effect on cell capacity was detected for rest periods (≥1 h).
- The influence of rest periods on the lifetime is insignificant.
- A long break is better for the lifetime than many short breaks between each cycle.

ARTICLE INFO

Article history:
Received 18 December 2012
Received in revised form
27 February 2013
Accepted 12 March 2013
Available online 30 March 2013

Keywords:
Lithium-ion cells
Lifetime
Electrochemical impedance spectroscopy
Rest period
Relaxation effect

ABSTRACT

The influence of rest periods on the lifetime of lithium-ion cells is investigated. The investigations focus on commercially available cells (type 18650) with a lithium–nickel–manganese–cobalt-dioxide (NMC)/lithium–cobalt-dioxide (LCO) blend and lithium–iron–phosphate (LFP) as cathode material and graphite as anode material. The above test cells are subjected to different cycle tests. Important influence factors in addition to the relaxation time are: the current, the temperature and the state of charge (SOC).

We were able to detect an increase of capacity (e.g. 0.1% of the nominal cell capacity for LFP test cells) after a rest period of 120 min in our measurements, the so called relaxation effect.

Further, the question is answered, whether relaxation affects battery lifetime. This was achieved by cycling cells with and without different rest periods at different temperatures and C-rates with a total of 50 test cells. However, no observable differences between cells with and without rest periods (≤2 h) were found. Moreover, experiments with many small breaks or one larger break showed that the duration of one continuous relaxation time is more important for the aging behavior, than the sum of rest periods. In addition, also impedance spectra were evaluated.

1. Introduction

At the moment, the automotive sector is on the edge of an historic switch from conventional to electric powered drive-trains. Three essential features will decide the success or failure of hybrid electric and electric vehicles (HEV, EV): utilization, cost and lifetime. All three are linked together and influence each other. Thus, just a combination of these properties to an optimum will lead to the gain. Especially, the change of lifetime through utilization is a critical part for the most important component of an electric power train, the lithium-ion battery.

However, numerous factors influence the lifetime of such a system. Whereas, the influence of external factor like temperature *T*, current *I* or state of charge (SOC) are topic of research [1], one parameter is rarely considered so far: relaxation time. It is well known, that the cells of a battery require a certain time to reach a steady state in terms of charge, concentration and temperature. However, this time depends strongly on operation conditions like cell loading or temperature as well as on the cell chemistry. Therefore, this study will investigate relaxation phenomena of commercial 18650 type lithium-ion cells as used in the Tesla Roadster [2] and even more their impact on lifetime under different operation conditions like *T*, SOC, *I*. In order to evaluate a potential influence, all cells are tested regularly by means of electrical parameter identification tests as well as by electrochemical impedance spectroscopy (EIS). Also, the effect of a multiplicity of short breaks versus long breaks is analyzed for different break durations. The different break duration, refers to the non-operational periods of the battery during its lifetime. Moreover,

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http://dx.doi.org/10.1016/j.jpowsour.2013.03.053

two different cathode materials – iron phosphate and nickel cobalt manganese – will be investigated in order to observe the influence of the cathode design on relaxation effects.

Three aims of this work can be distinguished: First, the detection of relaxation processes and identification of associated time scales and thus possible references to electrochemical processes. Second, statements about the dependency of lifetime on breaks and a description of these dependencies for the tested operation conditions. Third, possible consequences for the operation of HEVs, especially the interaction of the combustion engine and the battery in order to increase battery lifetime. HEVs are controlled by a given operation strategy and an intelligent algorithm will lead to a significant lifetime extension [3]. In addition, the development of accelerated aging tests by reduced break times is an interesting point. At the moment, cycle life test is accomplished by realistic break times, which can be up to 22 h per day for HEVs. However, the transferability and limit of the approach of shorten non-operational periods in such an accelerated aging test is unknown. Thus, knowledge about the interrelation of shortening and reducing lifetime would yield into significant savings of testing times and consequently costs.

2. Theory of cell degradation and relaxation processes

Various publications can be found about degradation processes in lithium-ion cells. An excellent analysis of the processes, divided into each cell component for all common lithium-ion chemistries is given by Vetter et al. [4]. It is shown that several processes take place at each component, leading to an increase of cell resistance as well as decreasing capacity. The main effects for lithium-ion cells seem to be the SEI [5–7] formation and reformation, electrolyte decomposition as well as corrosion and loss of active material. Various degradation effects on aged cells in HEV applications are investigated in Ref. [8]. Based on aging test data, calendar life and cycle life are investigated by considering resistance and capacity as the corresponding parameters. Moreover, the components are analyzed by multiple analysis techniques. Overall, it is identified that degradation for this case is mainly caused by inactive lithium, which is not available for charge transport anymore.

However, none of these works indicate the influence of relaxation on aging. In general three types of relaxation effects during breaks are conceivable:

I. Structure of a double-layer
II. Local concentration and charge equilibrium
III. Drop of concentration gradient in active material and electrolyte

All three relaxation phenomena start after the disconnection of the external current circuit. Different time constants can be observed similar to the ones of modeling by equivalent circuit models [9]. Whereas, the first process occurs in milliseconds interval, the second and third one can take up to hours as indicated in Fig. 1.

Looking at the different lithium-ion cell types, it is obviously that the intercalation process of ions depends strongly on the material property and structure. The active materials, especial the cathode materials can be divided into three categories regarding to their structure [10].

Cathodes with spinel structure like $LiMn_2O_4$ (LMO) are open from all dimensions and are therefore theoretically easier to access for ions, than olivine structures as $LiFePO_4$ (LFP), where the one-dimensional channels can be blocked during cycling. Therefore, two materials with different structures as well as open circuit voltage (OCV) curves will be used in this work. A second, also simple imaginable influence is given by the applied current

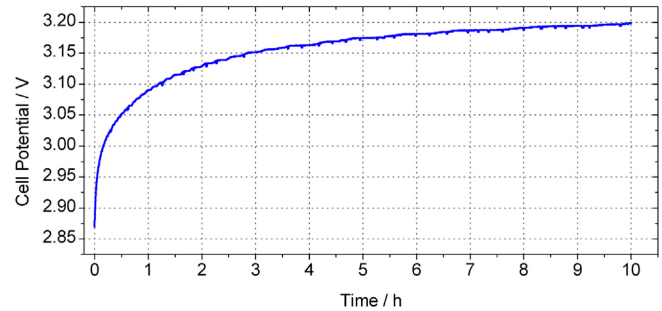

Fig. 1. Measured relaxation of cell voltage (NMC/LCO) after a 1 C discharge step (CCCV), measured at 20 °C.

amplitude and current duration. Evidence for this is given by J. Liu et al. [11]. They have measured the $FePO_4$ phase concentration versus the scan distance along the vertical direction of the electrode at 50% SOC charged at 20 mA g^{-1} (0.11 C) and at 3 A g^{-1} (18 C). These measurements were carried out using a synchrotron X-ray microdiffraction method.

As expected, for low currents a uniform charge balance and for high currents a concentration gradient is found. Thus, a sufficient charge excitation brings the system into an unsteady state, which should be detectable by relaxation processes. A third parameter is given of course by temperature. An equalization of the ions will mostly happen due to diffusion effects, which are strongly temperature dependent. Again, a reference to Fig. 1 is recommended, showing that even after hours no steady state is reached. Another interesting question is the source of relaxation. The simulation carried out by T. F. Fuller et al. [12] gives suggestions about the relaxation dominating electrode. In this simulation sufficient lithium-ion concentration equilibrium is given in the anode already after 6 min. In contrast, no equilibrium is found even after 34 min in the layered cathode. As a consequence, the relaxation periods in this work are placed at fully discharged cells with a SOC of 0% in order to gain a maximum relaxation effect. Additionally, identically tests were carried out with relaxation periods at 100% SOC in order to investigate the effect of the electrodes. The last important parameter is given by the duration of the break. But, not only the duration seems to be important, also the distribution of this duration is very interesting. It is unknown so far, if many short breaks, called micro breaks are more sufficient as few long breaks, called macro breaks for an extension of lifetime. Therefore, the influence of micro breaks versus macro breaks with the same total duration will be investigated and analyzed.

3. Experimental

Experiments were conducted on commercial available 18650 type cells. A 1.1 Ah graphite/lithium–iron–phosphate (LFP) high power cell and a 2.6 Ah graphite/lithium–nickel–manganese–

Table 1
Test cell parameter.

	NMC/LCO type	LFP type
Company	Samsung	A123 Systems
Labeling	ICR-18650-26F	APR-18650-M1A
Dimensions		
Length/mm	65	64.9
Width/mm	18.4	18.2
Electrical parameter		
Capacity/Ah	2.6	1.1
Nominal voltage/V	3.6	3.3
Max. charge voltage/V	4.2	4.2
Discharge cut off/V	2.7	2.7
Operating temperature/°C	−20 to 60	−30 to 60