Journal of Power Sources 392 (2018) 168–175

Contents lists available at ScienceDirect

Journal of Power Sources

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

Long-term cycling induced jelly roll deformation in commercial 18650 cells

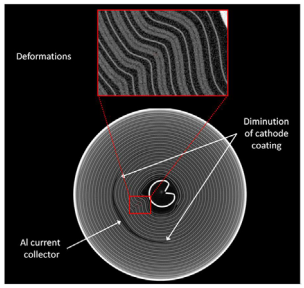
A. Pfrang[a], A. Kersys[a], A. Kriston[a], D.U. Sauer[b,c,d], C. Rahe[d], S. Käbitz[b,d], E. Figgemeier[b,d,*]

[a] European Commission, Joint Research Centre (JRC), Directorate for Energy, Transport and Climate, Energy Storage Unit, NL-1755 ZG Petten, The Netherlands
[b] Institute for Power Electronics and Electrical Drives (ISEA), RWTH Aachen University, Jägerstrasse 17-19, 52066 Aachen, Germany
[c] JARA-Energy, 52425 Jülich, Germany
[d] Helmholtz Institute Münster (HI MS), IEK-12, Forschungszentrum Jülich, Jägerstrasse 17-19, 52066 Aachen, Germany

HIGHLIGHTS

- Jelly roll deformations observed in Sanyo 18650 cells by X-ray CT after cycling.
- Deformations preferentially observed in the vicinity of the Al cathode tab.
- Post-mortem analysis showed that electrode delamination is linked to deformation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Lithium-ion batteries
Ageing
Post-mortem analysis
Micro X-ray computed tomography
Deformation
18650

ABSTRACT (MAX 200 WORDS)

The effects of extended charge/discharge cycling on the morphology of the jelly roll of commercial 18650 lithium-ion battery cells (Sanyo UR18650E) are shown and discussed. Using micro X-ray computed tomography combined with post-mortem analysis it is shown that the jelly roll exhibits significant deformations after charge/discharge cycling. This effect appears despite the presence of a solid inner pin, which had been suggested in literature as prohibitive for jelly roll deformation. The effect is related to an inhomogeneous architecture of the cells caused mainly by the cathode tab in the vicinity of which deformations were observed most often. While it is shown here that such deformations eventually lead to delamination of the otherwise rather stable cathode coating and cause a rapid capacity fade, jelly roll deformation has also been observed after more than 1700 equivalent full cycles on cells which show a typical, non-accelerated ageing behavior for this cell type. A correlation between occurrence of delamination and occurrence of deformation was clearly identified by combining post-mortem and computed tomography analysis. It is discussed, if the well-documented deformation is caused by thickness variations of the anode and cathode during charge/discharge cycles. Furthermore, an in-depth characterization of the cell design is documented.

1. Introduction

Since its first market introduction by Sony in 1991 [1], lithium-ion technology has turned into a disruptive battery technology finding applications in electronics, transportation and stationary storage industries world-wide. Lithium ion batteries with an overall capacity of more than 80 GWh were produced in 2016 with a significant growth rate year by year driven mainly by the automotive sector [2].

In parallel to the market penetration, the interest of developers and researchers increased significantly with performance degradation mechanisms and ageing of lithium-ion batteries receiving particular attention - understandably since degradation is highly relevant for all

* Corresponding author. Helmholtz Institute Münster (HI MS), IEK-12, Forschungszentrum Jülich, Jägerstrasse 17-19, 52066 Aachen, Germany.
E-mail address: e.figgemeier@fz-juelich.de (E. Figgemeier).

https://doi.org/10.1016/j.jpowsour.2018.03.065
Received 20 October 2017; Received in revised form 13 January 2018; Accepted 25 March 2018
0378-7753/

applications and is a crucial consideration for the introduction of new materials. In-situ and ex-situ investigations using numerous analytical techniques were published over the last more than 20 years clarifying degradation mechanisms in lithium-ion battery cells. Therefore, a solid understanding of the dominating factors for degradation has been reached [3–8,29]. Nevertheless, continuously changing cell designs with improved performance in energy density and power density raise new questions in regard to degradation. It is by far not possible to fully predict the impact of a new component or the change of the morphology of the electrodes on battery lifetime and reliability. Therefore, establishing new techniques for predicting performance degradation and an even better understanding of structure-activity relationship for lithium-ion batteries is mandatory.

While the ever changing chemistry and materials of lithium-ion battery cells are typically considered in degradation investigations by academic groups, aspects of particular structural features in commercial cells are not sufficiently taken into account. Namely, degradation caused by the presence of geometrical inhomogenies such as tabs, tight bends of the electrodes, or effects of the anode surplus present in most cells for preventing lithium plating [9]. In the majority of published investigations, either lab cells or a small number of commercial cells were the focus of attention. Large systematic studies considering time frames of several years and accordingly several thousands of charge/discharge cycles are rather rare despite the commercial relevance of long-lived battery systems. In this context, a comprehensive calendar and cycle life study examining the ageing mechanism of a large number of 18650 cells (Sanyo, 2.05 Ah, labeled UR18650E) were performed and published [10]. The detailed test matrices of both analyses are described in Refs. [10] and [11]. The calendar life tests focused on the influence of the state of charge (SoC) on ageing, while cycle life tests investigated the influence of cycle depth and mean SoC on ageing. The cycle tests study revealed two major findings [11]: First, the negative electrode potential influences the degradation rate of the cell: Cycling around a mean SoC of 50% was found to be the optimum point regarding lifetime, while cycling around higher and lower mean SoCs, showed accelerated degradation. The authors suggested that mechanical stress induced during cycling between different voltage plateaus is a reason for faster degradation. Second, cycle depth has a linear impact on capacity fade. The calendric ageing tests indicate that storing cells at high SoCs accelerates ageing [10]. Some cells showed a 'sudden death' – an accelerated decline of the capacity – mostly at the point where 20 % of the initial capacity was lost and the internal resistance mounted to over 150 % of the initial value.

OCV and EIS studies were also performed on these 18650 cells focusing on the ageing of the cell [12]. Crumbling off of the anode coating observed during post-mortem analysis indicated very poor adhesion. However, this feature cannot be expected to be the main reason for the ageing process, because very little capacity loss was observed during the cycling tests. This suggests that the mechanical confinement within the cell is sufficient for keeping the graphite material in electrical contact within the anode layer and with the Cu current collector. Nevertheless, when removing the electrode from the can, the material did not stick any longer to the current collector.

The reason for observed sudden failures, which occurred apparently randomly with a large spread of cycle numbers could not be explained conclusively by the performed investigations. It is not fully clear, if e.g. clogging of the anode pores caused by parasitic reactions at the cathode as suggested by Dahn et al. caused the rapid failure of the Sanyo 18650 cells as described in the earlier studies [7,12].

In this work we intended to further analyze failure of the Sanyo 18650 cells in order to complement the already published investigation with the goal to achieve a comprehensive and complete understanding of the degradation of the cell. Micro X-ray computed tomography (CT) has been applied successfully on battery cells for the non-destructive analysis of cell structure [13–16,30]. Such analysis is available at synchrotron sources, but also lab-based stand-alone CT systems have become rather wide-spread in the recent years. CT is especially useful for the examination of damaged cells [15,17,18] and can also facilitate post-mortem analysis by providing guidance for the disassembly process [5,19]. Even CT of a cell during thermal runaway has been demonstrated at a synchrotron [6]. In this work, computed tomography and post-mortem analysis have been applied to a selection of the Sanyo cells to correlate electrochemical data with morphological observations.

2. Experimental

2.1. Ageing – electrochemistry, equipment, methods

For the ageing investigation high energy 18650 lithium-ion battery cells manufactured by Sanyo, labeled UR18650E have been used. The cell is designed for automotive application and has a nominal capacity of 2.05 Ah. Voltage between 2.5 and 4.2 V is allowed by the manufacturer, with a nominal voltage of 3.6 V. The gravimetric energy density of the system is about 165 Wh kg^{-1}. The materials comprise graphite in the anode and $Li(NiMnCo)O_2$ in the cathode. All cells were cycled at 1C rate, 33 °C at various DoD[1] and SoC levels. In total, 9 cells with different ageing histories were investigated by CT imaging (see Table 1). The end of life criterion for testing was defined as reaching less than 80 % of the initial capacity, some cells were further cycled for analysing further ageing effects. The actual SoCs relate to the OCV curve, so a CC/CV charge was used to reach the mentioned SoC. During testing the cells were charged and discharged Ah-based and adjusted during check-up to the mean SoC via CC/CV charging. The actual cell capacity was defined as the charge capacity (CC to 4.2 V/CV till the current decreased to less than 0.02 C) [10]. The number of equivalent full cycles was calculated by dividing the overall charge provided by the cell over all cycles by the nominal battery capacity.

2.2. Micro X-ray computed tomography (CT)

A Nanotom S X-ray computed tomography system (GE Sensing & Inspection Technologies, phoenix x-ray, Wunstorf, Germany) was used. The system is equipped with an X-ray tube with a maximum output power of 15 W and a maximum high voltage of 180 kV in combination with a 2D detector with a dynamic range of 850:1 which consists of 2300 × 2300 pixels. An X-ray energy in the range of 110–140 kV was selected. A voxel size of 32 µm was used for imaging the complete cell (in the following referred to as 'low resolution') and a voxel size of 5 µm for 'high resolution' imaging. 2000 projections were imaged for each dataset for low resolution and 3700 for high resolution using the full pixel resolution of the detector. For high resolution, the size of the detector was virtually enlarged by a factor of two by moving the detector horizontally (for each projection two images were subsequently stitched together automatically).

Dedicated software – VG Studio MAX (Volume Graphics, Heidelberg, Germany) – was applied for data visualisation and analysis. In the presented CT gray-value cross-sections, brighter corresponds to higher X-ray absorption (e.g. metal casing with its higher density appears brightest compared to other materials).

2.3. Layer thickness measurements

Visibility of a certain structural feature in CT depends not only on contrast difference – X-ray absorption – with the surrounding material, but also on the size of the structural feature compared to spatial resolution of the measurement. In order to ensure a sufficient accuracy, layer thickness measurements were only performed on 'high resolution'

[1] The cells were cycled around the SoC with the DoD. E.g.: Cell S005 was cycled from 85 to 95% SoC.