

Nonlinear aging of cylindrical lithium-ion cells linked to heterogeneous compression



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ABSTRACT

Second-life applications of automotive lithium-ion batteries are currently investigated for grid stabilization. Reutilization depends on reliable projections of the remaining useful life. However, reports on sudden degradation of lithium-ion-cells near 80% state of health challenge these extrapolations. Sudden degradation was demonstrated for different positive active materials. This work elucidates the cause of sudden degradation in detail. As part of a larger study on nonlinear degradation, in-depth analyses of cells with different residual capacities are performed. Sudden degradation of capacity is found to be triggered by the appearance of lithium plating confined to small characteristic areas, generated by heterogeneous compression. The resulting lithium loss rapidly alters the balancing of the electrodes, thus generating a self-amplifying circle of active material and lithium loss. Changes in impedance and open-circuit voltage are explained by the expansion of degraded patches. Destructive analysis reveals that sudden degradation is caused by the graphite electrode while the positive electrode is found unchanged except for delithiation caused by side reactions on the negative electrode. Our findings illustrate the importance of homogeneous compression of the electrode assembly and carbon electrode formulation. Finally, a quick test to evaluate the vulnerability of cell designs toward sudden degradation is proposed.

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1. Introduction

Lithium-ion batteries are the most advanced technology for energy storage devices due to their high energy density and efficiency [1,2]. In various fields such as consumer devices or electrified vehicles, lithium-ion technology enables new applications. The current uncertainty regarding the reachable use time inhibits deeper market penetration. Reports in literature about suddenly increasing aging rates raise concern regarding the viability of aging models and their use in lifetime projections [3–5]. In this work, the aging effect is investigated in detail. Probable root causes are presented. Furthermore, design imperfections and use conditions leading to such unfavorable behavior are discussed as well.

Lithium-ion battery aging is a complex process with several influencing degradation mechanisms as shown by recent studies on commercial batteries [3,4,6–11]. For conciseness, only the main

influence factors are discussed here since recent reviews [12–14] already provide a broad view on aging processes. In aging models, the capacity fade is mainly attributed to the formation of passive films, leading to lithium loss and resistance increase, as both negative and positive electrodes are usually operated outside the electrolyte's electrochemical stability window [12]. Lithium loss is generally attributed to the solid electrolyte interphase (SEI) on the negative electrode, while passive films on the positive electrode are associated to rising resistance. Studies on electrolyte aging have shown the impact of carbonate and LiPF₆ decomposition [15–19] as well as the mitigating effects of additives [20,21]. The calendric capacity fade resulting from passive film formation has been shown to have a square root dependency on time [4,10,13,22,23]. Nearly linear aging behavior has been reported to be influenced by additional aging factors [3]. It is usually reported that cyclic aging causes linear fading of capacity and square root dependencies on charge throughput are sometimes reported as well [3,13,24,25]. SEI formation, causing lithium loss and increasing resistance, is reported to be the dominant source of capacity fade. The linear aging model may be used for projections of SEI growth and residual value of aged cells and battery packs, but

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reports on suddenly increasing aging rates put such projections into question [3,4,26]. The inflection point has been linked to partially irreversible lithium plating [4]. The occurrence of inactive lithium, which is not stripped upon full discharge of the cell, is noteworthy as it shows the possibility of irreversible capacity loss due to local disconnection of parts of the electrodes' electrochemically active materials. While counterintuitive, incomplete stripping of lithium metal is a well-described effect of the solid electrolyte interphase [27–30] and has been shown to lead to effective loss of lithium on model substrates [31,32] and on graphite electrodes in cycled batteries [14,33–36]. Also in this study, we found inactive lithium on the nearly totally delithiated graphite electrode despite the potential difference of more than 0.5 V. As inactive lithium is not in electrical contact to the electrode, it is difficult to detect by electric means, while it is easily detected by post-mortem observation.

In a recent article [37] the regimes leading to sudden degradation in lithium-ion batteries are investigated on cell level. Control regimes causing sudden degradation are identified and guidelines for avoidance are given. The identified factors leading to the sudden degradation of usable capacity are high depth of discharge, high charging currents and low temperatures. Cells cycled between 3.0 V and 4.2 V with constant current charging at 0.5 C and constant current discharging with 1 C exhibited normal behavior up to 800 equivalent full cycles as shown in Fig. 1. Based on the observed behavior it appears reasonable to predict several hundred additional cycles above 60% residual capacity. However, a sudden increase in degradation rate occurs at about 80% residual capacity. Only 150 cycles later the cell has lost more than half of its initial capacity.

In this work, we investigate cells exposed to this cyclic aging protocol at three different stages of aging. Expanding upon previous work, we deliver an insight into the chemical changes inside the cells from which the behavior was described before [37]. Uncycled, pristine cells (A) are compared to cycled cells that have just started to increase their aging rate (B) and cells that have already degraded significantly (C). Causes and effects are investigated in detail. Using destructive analysis, so called post-mortem studies, cells are characterized on the component level by electrochemical methods and chemical analyses. The influence of cell design on aging is discussed. Furthermore, possible mechanisms of sudden rapid aging are explained on component level. Moreover, the reasons for sudden degradation, as well as design and control countermeasures are explained. Finally, a quick test for the vulnerability of cell designs toward nonlinear degradation is proposed.

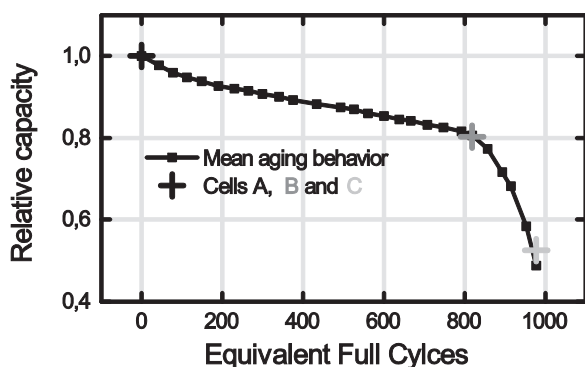


Fig. 1. The cells show a strong increase in aging at about 80% residual capacity. Cells are further analyzed in uncycled state (A), as they just start to age faster (B) and after the kink in capacity (C).

2. Experimental

In this study, lithium-ion cells with lithium–nickel–manganese–Cobalt oxide (NMC) based positive and graphite based negative electrodes were investigated. The cylindrical Molicel IHR18650A by E-One Moli Energy Corp. has a nominal capacity of 1.95 Ah. Cells called pristine in this article have undergone formation procedures at the discretion of the manufacturer. The utilized instruments are listed in Table 1.

Cells A–C were obtained from a large aging experiment [37]. In this study they were cycled with constant current between 3.0 V and 4.2 V. Charging was carried out at 0.5 C and discharging at 1 C.

For a quick test to evaluate the vulnerability toward plating and for thermography a constant current, constant voltage scheme was used for both charge and discharge procedures to exert maximal stress. For control experiments in Sections 3.3 and 3.4, the charging current was chosen to be 1 C, while the discharge current was set to 2 C. Constant Voltage steps at 3.0 V and 4.2 V were maintained until the current dropped below 0.1 C for more than one second. Ambient temperature was held at 20 °C.

Prior to destructive analysis, cells were characterized with a 0.02 C full cycle between 3.0 V and 4.2 V, as well as a checkup procedure as described in our previous work [37]. The 18650 cells were discharged to 3.0 V with a constant voltage step held until the current dropped below 0.1 C. Then, the cells were opened in a glovebox with controlled argon atmosphere.

Preparation for electrochemical analysis and scanning electron microscopy (SEM) was entirely carried out under argon and samples for SEM were transferred under vacuum without washing steps or contact to air using a custom sample holder. Samples for inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray diffraction (XRD) were handled in air.

Samples for ICP-OES from both negative and positive electrodes were taken, washed and dried under argon atmosphere. Washing was performed by soaking samples in dimethyl carbonate (MERCK SelectyLite™) for 60 min, renewing the dimethyl carbonate solution and soaking for another 30 min. The samples were then dried under vacuum using the antechamber of the glovebox and weighted under argon atmosphere. Samples were then exposed to air and dissolved using *aqua regia*. *Aqua regia*, a strong oxidizing acid, was obtained by freshly mixing three volume parts of concentrated hydrochloric acid (fuming 37%, for analysis, MERCK) with one volume part of concentrated nitric acid (concentrated 65%, p.a., Th. Geyer). The samples were stirred in *aqua regia* overnight. All metal parts and active materials were oxidized and dissolved so that only graphite and binder remained as solid residue. The solid residue was filtered off and weighted. The obtained clear solutions containing the metal species were then analyzed by ICP-OES. ICP-OES-measurements were run using a glass cyclonic-action spraychamber with glass concentric nebulizer for the sample introduction and a radially viewed plasma. The interpretation of signals was performed using repeat measurements of samples and calibration standards prepared in 1% hydrochloric acid. The wavelengths used for the analysis of element concentrations are shown in Table 2. The output was averaged over all monitored wavelengths.

Using a custom-built computer tomograph based on a 225 kV X-ray tube, flat panel detector and rotary sample stage, complete volume information of pristine cells of the same type was reconstructed. XRD of positive electrode samples was performed under air.

Temperature gradients were investigated by thermal imaging. As the battery was covered by polymer based shrink wrap, its emissivity was estimated to be 0.95. Thermal images and temperature values from three points on the surface were collected while the battery was cycled.

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