Inhomogeneous degradation of graphite anodes in automotive lithium ion batteries under low-temperature pulse cycling conditions

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HIGHLIGHTS

- Low temperature pulse cycling induces fast aging due to lithium plating.
- Charged and discharged anodes are studied.
- XRD reveals inhomogeneous intercalation phase distributions.
- Plated and intercalated lithium is distributed inhomogeneously over the anode.
- Lithium is plated in partly reversible thick surface deposits.

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ABSTRACT

The aging of graphite anodes in prismatic lithium ion cells during a low temperature pulse charging regime was studied by electrical tests and post-mortem analysis. The capacity decrease and impedance increase mainly occurs in the beginning of cycling and lithium plating was identified as the major aging mechanism. The degradation and the local states of charge show an inhomogeneous distribution over the anode, which is confirmed from spatially resolved XRD studies and SEM combined with EDX performed on electrode cross sections. Comparing a charged cell with a discharged cell reveals that ca. 1/3 of the lithium is plated reversibly at the given SOH of 60%. It is proposed that high charge rates at low temperatures induce inhomogeneities of temperature and anode utilization resulting in inhomogeneous aging effects that accumulate over lifetime.

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1. Introduction

Lithium ion batteries are nowadays the preferred energy storage device for plug-in hybrid (PHEV) and battery electric vehicles (BEV) [1]. State-of-the-art automotive lithium ion batteries contain graphite based anodes and layered lithium nickel manganese cobalt oxides (NMC) cathodes. Providing a high energy and power density and a good cycle life, this cell chemistry meets the requirements of automotive application. However, under prolonged cycling as well as storage the graphite anode can undergo several different degradation processes all leading to irreversible capacity loss. The capacity fade and underlaying processes strongly depend on operation parameters such as temperature, current rate and depth of discharge [2–4].

A very critical mode of operation is charging with high C-rates at low temperatures. In this condition the anode potential can drop below the potential of lithium metal. This induces deposition of metallic lithium on the anode surface, which is referred to as lithium plating and was described in several works [5–11]. It is considered to be the dominant aging mechanism, when fast charging protocols are applied [12,13].

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Lithium plating can be caused either by charge transfer limitation due to high charging rates or by solid state diffusion limitation due to low temperature [14]. Being re-oxidized at a potential of about 100 mV, plated lithium should in principle disappear during discharge [8]. However, loss of electrical contact or passivation through the formation of high-impedance surface films can lead to irreversible deposition creating "dead lithium". Thus, lithium plating can cause severe irreversible capacity losses. Additionally, lithium can form dendritic crystallites that may cause internal short circuits by penetrating the separator membrane [15,16].

In fact, lithium plating is strongly dependent on local electrode properties, like temperature and current density that can be distributed quite inhomogeneously in a large-scale cell containing several meters of electrode foil. Therefore, we see a need to study degradation not only at lab-scale, but also in cells close to application. Whereas most of the studies make use of small, lab-scale test cells, only little is known about low-temperature aging of large-scale automotive cells. Waldmann et al. assumed lithium plating to be the main cause for 18650-type cell aging, but were not able to characterize it in a post mortem analysis [17]. Bitzer, Gruhle and Veth observed lithium plating in pouch cells for automotive application [9,18]. Petzl et al. recently presented a study of lithium plating in prismatic cells. They found a smaller amount of plated lithium in the inner compared to the outer part of the electrode jelly roll and related it to a mechanical pressure increase due to a smaller winding radius [7].

As design aspects also influence the thermal properties of the cell, this may have an influence on degradation as well. Both thermal modelling and thermal imaging studies indicate inhomogeneous temperature distributions in large format cells, especially when external cooling is applied [19–22]. We assume that at low temperature and high charging rates (a) lithium plating is the major degradation effect with all others being negligible and (b) thermal effects are dominating over mechanical influences and local spot inhomogenities. Provided these assumptions are true and regarding the before mentioned thermal studies, degradation inhomogenities should occur perpendicular to the winding direction of the jelly roll, coinciding with thermal inhomogenities.

In this work prismatic lithium ion cells for automotive application were aged at low temperature by high current pulse charging. The pulse charging regime was chosen to maintain a high average charging rate [23,24]. In a conventional constant current/constant voltage charging procedure the major amount of charge would be transferred during the constant voltage phase at reduced currents. In order to follow the degradation in-situ, impedance spectroscopy is applied. A simple model is applied to derive parameters that are able to describe the degradation process. A Post-Mortem analysis is carried out afterwards in the discharged as well as in the charged state. Thus, it is possible to study the occurrence of both reversible and irreversible lithium plating. We present methods for thickness measurement of plated lithium and for spatial resolved state-of-charge estimation. The techniques applied for material analysis are XRD, SEM, EDX and Raman spectroscopy.

2. Experimental

2.1. Electrical tests

The investigated cells are commercial prismatic Lithium-Ion cells in the PHEV2 format with a nominal capacity of 25 Ah. The anode consists of graphite as active material mixed with carbon black and a SBR/CMC-based binder and coated on copper foil. The layer thickness is ~60 μm. The cathode consists of a $Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O_2$ active material mixed with carbon black and a PVDF-based binder and coated on aluminum foil. An EC/DMC-based electrolyte with $LiPF_6$ as conducting salt and a PE/PP-separator membrane is used.

The following electrical tests were performed:

a) Performance measurement

During cell aging the performance was tested at 23 °C. To maintain constant thermal conditions the cells were tempered for 3 h before the tests. The cells were charged at 1C to 4.1 V, followed by a constant voltage phase until the current dropped to C/20. After a rest period of 30 min the cells were discharged at 1C till 2.5 V, followed again by 30 min rest time. This procedure was repeated for 5 cycles and the last discharge capacity is used for comparison and state-of-charge adjustment. The cells were then fully charged again as described and impedance spectra were recorded at 100/80/75/70/65/50/35/20/10%SOC. After each SOC adjustment a rest time of 30 min was applied before the impedance measurement was performed from 5 kHz to 10 mHz with an amplitude of 2 A.

b) Rapid-aging test by pulse-charging at −15 °C

After tempering at −15 °C for 3 h the cells were repeatedly charged at 8C for 15 s followed by 5 s rest time. During each pulse the current is reduced in a constant voltage phase, as soon as the voltage reached 4.1 V. When the current dropped down to 1C, the cell was defined as fully charged. After a rest period of 10 min the cells were discharged at 2C to the lower voltage limit of 2.5 V. After another rest time of 10 min the first cycle was completed and the procedure was repeated. After every 25 cycles a performance measurement was carried out.

2.2. Cell opening and sample preparation

Cell opening was performed in an argon filled Glovebox with a water content of <0.1 ppm and an oxygen content of <5 ppm in the atmosphere. Materials characterization was performed after different sample preparation procedures depending on the characterization method:

- SEM and optical microscopy: Unwashed samples.
- EDX: Ca. 0.5 cm^2-sized sample fragments were rinsed with two drops of DMC.
- Raman: Samples were washed in DMC in a Soxhlet device for several cycles.

Electrode cross sections for SEM/EDX analysis were prepared by ion beam cutting using a Hitachi IM400 ion milling device. Argon ions accelerated with 4 kV were applied. Charged samples were prepared using an encapsulation to avoid any air contact. Cross sections for Raman measurements were cut with a very sharp scissor to avoid ion beam caused damages.

2.3. Material characterization

For -cell measurements disc electrodes of 13 mm diameter were prepared from the harvested anode material. As the active mass was very brittle, the backside of the double-sided electrode foil was not removed. Instead, the disc electrode was contacted from the coated backside and the high internal resistance was taken into account by applying low C-rates. Other cell components were freshly ground lithium metal used as a counter electrode, Whatman glass fiber sheets used as a separator and Merck LP30 type battery electrolyte. The cells were tested with a BaSyTec CTS battery test device. The anode was delithiated at C/20, C/100 and C/1000 to an end-of-charge-voltage of 2 V, intermitted by breaks of 5 min.