



Post-mortem analysis on LiFePO₄/Graphite cells describing the evolution & composition of covering layer on anode and their impact on cell performance



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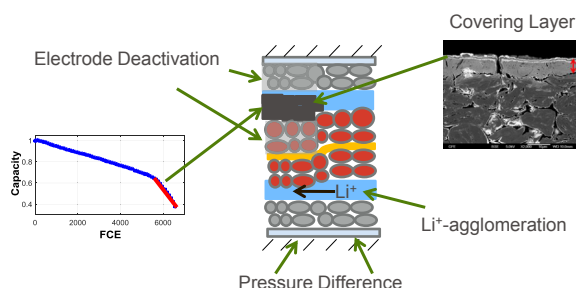
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HIGHLIGHTS

- Covering layer is present for cyclic aged cells.
- Covering layer is on top of the anode facing the separator.
- Covering layer consists of SEI products and metallic lithium.
- Charge agglomeration under local pressure on the jelly role.
- Deactivation of electrode occurs for dense covering layer.

GRAPHICAL ABSTRACT



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ABSTRACT

During cyclic aging of lithium-ion batteries the formation of a μm -thick covering layer on top of the anode facing the separator is found on top of the anode. In this work several post-mortem analyses of cyclic aged cylindrical LFP/Graphite cells are evaluated to give a detailed characterization of the covering layer and to find possible causes for the evolution of such a layer. The analyses of the layer with different methods return that it consists to high percentage of plated active lithium, deposited Fe and products of a solid electrolyte interphase (SEI). The deposition is located mainly in the center of the cell symmetrical to the coating direction. The origin of these depositions is assumed in locally overcharged particles, Fe deposition or inhomogeneous distribution of capacity density. As a secondary effect the deposition on one side increases the thickness locally; thereafter a pressure-induced overcharging due to charge agglomeration of the back side of the anode occurs. Finally a compact and dense covering layer in a late state of aging leads to deactivation of the covered parts of the anode and cathode due to suppressed lithium-ion conductivity. This leads to increasing slope of capacity fade and increase of internal resistance.

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1. Introduction

This contribution summarizes the findings of the cell tests on 50 cylindrical 8 Ah LFP/Graphite and additional post-mortem analyses

Abbreviations

FCE	full cycle equivalents
DVA	differential voltage analysis
CDA	capacity difference analysis
PMA	Post-mortem-analysis
EC	ethylene carbonate
DMC	dimethylene carbonate
EMC	ethylene-methylene carbonate
DEC	diethylene carbonate
LFP	lithiumironphosphate
SEI	solid electrolyte interphase
DOD	depth-of-discharge
SOC	state-of-charge
EIS	electrochemical impedance spectroscopy
HF	hydrofluoric acid
CMC	carboxymethyl cellulose
SBR	styrene-butadiene rubber
PVDF	polyvinylidene fluoride

(PMA) to describe the evolution and the influence of a dense covering layer on top of the anode facing the separator. The dense covering layer is found exclusively for cells aged in cycle tests. Therefore, the covering layer cannot be described solely by calendar aging effects as reported e.g. by Kassem et al. [1].

The degradation of the cells is analyzed with different methods. In Ref. [2] the trends of capacity and internal resistance for these cells are discussed. The covering layer was only found for cyclic aged cells but not for calendar aged cells [3] which is in good accordance to literature [4–6]. The covering layer on top of the anode facing the separator is reported for the following cathode materials: LiFePO_4 [2,4,5] and $\text{LiMn}_2\text{O}_4/\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})\text{O}_2$ [6].

The covering layer of the discussed cells was not found for all test conditions and equally tested cells did not necessarily show the same deposition pattern [3]. Therefore, the deposition is assumed to be most likely additionally influenced by the homogeneity of the coating in form of bad contacted particles or inhomogeneous distribution of capacity density. This conclusion is supported by the fact that the deposition was always found in direction of winding or coating at the center or the edges of the electrode's height, respectively [2,3]. Other constraints that are related to the winding direction are temperature and pressure. Those two parameters are further increasing towards the cell's center due to increasing friction and higher distance to the colder housing. This becomes crucial especially for cycling at high C-rates.

Strong inhomogeneities induced e.g. by the evolution of covering layer are detectable with the capacity difference analysis (CDA) which is a non-destructive method to evaluate the difference of capacities measured at 1C and 0.25C [3]. If the capacity difference shows a strong rise during aging, the evolution of a covering layer is associated. This is supported by evaluating the differential voltage analysis (DVA) as it is shown in Ref. [7]. Here increasing inhomogeneity and loss of anode active material could be associated to the evolution of a covering layer. Furthermore, there are publications that found a correlation between the formation of covering layer with the increase of impedance and loss of active lithium [5,6].

The morphology of the deposition is depending on core temperature of the cell, the applied C-rate and the voltage regime of the cycling [3]. There seems not to be an intuitive and simple C-rate dependency, as the cycling at higher C-rates of 4C and 8C did not

lead to a dense covering layer whereas for 1C and 2C partially a covering layer could be observed. Since the C-rate gets along with resistive heat, the temperature might play a key role, too. An interesting finding is that the 1C cycling with the lowest DOD between 45 and 55% SOC at 40 °C leads to strong formation of covering layer, although the charge cut-off voltage is far away reducing risk of plating and nearly no volume expansion that may affect active material is expected. The evaluation of DVA leads to the assumption that due to the flat voltage curves of anode and cathode cycling induced inhomogeneous distribution of active lithium is not compensated under these test conditions. Thus, during the following check-up plating is likely [7].

The covering layer is discussed as a solid-electrolyte interphase (SEI) or something that is in conjunction with passivated lithium plating. This is assumed as it is not found surrounding the graphite particle, which would be expected for calendar aged cells. According to Klett et al. [4] for $\text{LiFePO}_4/\text{Graphite}$ the covering layer is rich in P-O bonds and contains Fe and carbonate species. Finally according to Klett et al. [4] the residual composition is similar to the SEI of a calendar aged cell.

In this contribution the formation of covering layer is discussed on behalf of three aged cells. Therefore, the morphology, the chemistry and the electro-chemistry are examined and linked to the full cell test results. Special focus is put on the causes leading to covering layer evolution on the primary and on the secondary side of the double-coated anode. The primary side is defined as the side where the covering layer evolution initially takes place. Finally the theory of deactivation of anode and cathode due to an impermeable covering layer will be proved by too high amount of lithium on the cathode and by geometrical approach considering the deactivated electrode area to explain the superposed capacity loss and internal resistance increase.

2. Experimental

2.1. Cell, aging and check-ups

The detailed description of the cells and the aging is already given in Ref. [2] and only a short excerpt is given here.

The tested cell is a cylindrical 8 Ah cells with LiFePO_4 (LFP) on the cathode, graphite on the anode and (EC-DMC-DEC-EMC)- LiPF_6 as electrolyte. The tests are performed at 40 °C temperature of the cell's case in a temperature chamber. The DODs of partial cycles are related to the nominal capacity. After a complete charge the mean SOC of 50% of the corresponding cycle, defined using the current capacity, was approached Ah-based. This is necessary as approaching voltage-based is difficult since LiFePO_4 is featured by a very flat open circuit voltage (OCV) curve.

Three aged cells were tested under the following conditions: 1C 45–55% SOC, 1C 0–100% SOC and 2C 25–75% SOC. After end of test a covering layer was observed in all three cells by using PMA.

The check-ups are performed at a chamber temperature of 25 °C between 2.0 V and 3.65 V. The capacity is measured at 1C and a low current cycle is performed at 0.25C used for CDA and DVA. Additionally, a 10 s-discharge-pulse at 50% SOC is evaluated.

2.2. Post-mortem analysis

The post-mortem analyses are performed under argon atmosphere in a fully discharged or fully charged state. The cells are evaluated by their surface morphology and color using a Keyence VK-9710 laser microscope (confocal microscope).

Scanning electron microscopy (SEM) results were obtained on a JEOL JEM-7001F, with an EDX detector from EDAX. The SEM was mainly used at a low energy (5 kV), in order to increase the surface

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