Aging behavior of lithium iron phosphate based 18650-type cells studied by *in situ* neutron diffraction

Neelima Paul [a, *, 1], Johannes Wandt [b, 1], Stefan Seidlmayer [a], Sebastian Schebesta [c], Martin J. Mühlbauer [a, d, e], Oleksandr Dolotko [a], Hubert A. Gasteiger [b], Ralph Gilles [a]

[a] *Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, 85747 Garching, Germany*
[b] *Chair of Technical Electrochemistry, Technische Universität München, 85748 Garching, Germany*
[c] *VW-VM Forschungsgesellschaft mbH & Co. KG, 73479 Ellwangen, Germany*
[d] *Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*
[e] *Helmholtz-Institute Ulm for Electrochemical Energy Storage (HIU), P.O. Box, 76021 Karlsruhe, Germany*

HIGHLIGHTS

- Aging in MCMB/LFP and NC/LFP cells was investigated by neutron diffraction.
- NC/LFP cell lost capacity on storage whereas the MCMB/LFP cell showed no loss.
- After 4750 cycles, the relative capacity losses were much lower for the MCMB/LFP cell.
- Entire capacity loss upon formation, cycling and storage is due to active lithium loss.
- Structural degradation and active material isolation could be excluded.

ARTICLE INFO

ABSTRACT

The aging behavior of commercially produced 18650-type Li-ion cells consisting of a lithium iron phosphate (LFP) based cathode and a graphite anode based on either mesocarbon microbeads (MCMB) or needle coke (NC) is studied by *in situ* neutron diffraction and standard electrochemical techniques. While the MCMB cells showed an excellent cycle life with only 8% relative capacity loss (i.e., referenced to the capacity after formation) after 4750 cycles and showed no capacity loss on storage for two years, the needle coke cells suffered a 23% relative capacity loss after cycling and a 11% loss after storage. Based on a combination of neutron diffraction and electrochemical characterization, it is shown that the entire capacity loss for both cell types is dominated by the loss of active lithium; no other aging mechanisms like structural degradation of anode or cathode active materials or deactivation of active material could be found, highlighting the high structural stability of the active material and the excellent quality of the investigated cells.

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1. Introduction

Since their commercialization by Sony in 1991, Li-ion batteries have become the main power source for portable consumer electronics. Due to their constant improvement in terms of cost, energy density and lifetime [1,2], Li-ion batteries have also started spreading into new markets like hybrid electric (HEV) and electric vehicles (EV) or grid storage within the last couple of years [3,4]. To be cost competitive with other energy storage technologies, the lifetime of Li-ion cells is a critical value: while a life time of 2–3 years is sufficient for most consumer electronic applications [5], a lifetime of 15 years and cycle life over 1000 charge/discharge cycles are required for battery electric vehicles (BEVs) [6]; even longer cycle life of over 5.000–10.000 charge/discharge cycles is required for grid storage applications [7]. In order to reach these targets, a detailed understanding of the undesired side reactions contributing to capacity fading is mandatory. Recently, a broad variety of analytical techniques has been used to unravel the underlying

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chemical, physical and mechanical processes taking place during charge, discharge (cyclic aging) and storage (calendar aging) of Li-ion batteries [8]. For many of these analytical techniques, *in situ/in operando* setups have been developed which offer several advantages in comparison to *ex-situ* analysis: i) enabling the detection of unstable reaction intermediates [9] or phases [10], ii) avoiding the risk of altering the sample, e.g., the state of charge or the oxidation state, during sample preparation [11], and iii) offering the possibility to continue with cell cycling following the analysis. Most spectroscopy and microscopy based *in situ/in operando* techniques require special cell designs which are transparent for either electromagnetic waves, magnetic fields, and/or electrons [12–15], thus rendering them unsuitable for the investigation of commercial Li-ion cells with generally impenetrable metal casing/housing. There are, however, degradation mechanisms which can only be studied in large-format cells, e.g., effects related to current collector tab positioning [16], cell geometry [17], or inhomogeneous heat distribution [18,19]. A powerful analytical technique for the *in situ/in operando* study of commercial Li-ion cells is neutron diffraction. Rietveld analysis of neutron diffractograms can be used to determine the atomic structure, lattice parameters, and particle size of crystalline anode (e.g. graphite) and cathode active materials (e.g. spinels, layered metal oxides, or phospho-olivines). In this respect, an important advantage of neutron diffraction over X-ray diffraction (XRD) is the higher penetration depth of neutrons in comparison to X-rays, making neutron diffraction truly bulk sensitive and suitable for large cell formats, whereas XRD is only suitable for thin samples [20]. Furthermore, neutron diffraction shows a much higher sensitivity for light elements like lithium than XRD.

Only few *in situ/in operando* neutron diffraction studies on commercial Li-ion cells have been published so far, typically based on cells with graphite anodes and a variety of cathode active materials like $LiCoO_2$ (LCO) [16,21–24], $LiMn_2O_4$ (LMO) [25], $LiMn_{0.33}Co_{0.33}Ni_{0.33}O_2$ (NMC) [10,16,26,27], and $LiFePO_4$ (LFP) [16,28–30]. These have focused on topics like structural changes within the cathode active material [22,26], metal doping [29,30], local inhomogeneities [16,25,31], or lithium plating on graphite [27]. While there are neutron diffraction studies on cell aging for commercial graphite/LCO cells [23,24], to the best of our knowledge no such data is available for graphite/LFP cells.

In this work, we carry out a detailed investigation of the aging mechanism in commercially produced 18650-type cells with a graphite/LFP cell chemistry. A total of four cells are investigated in this study which differ either in the type of graphite used as anode active material − mesocarbon microbeads (MCMB) versus needle coke (NC) - or in the cell history. One cell of each graphite anode material was cycled for 4750 cycles at a C-rate of 1 h^{-1} at 23 °C and one cell was stored for about two years at 20% state-of-charge (SOC) at 23 °C. For all four cells we systematically compare the electrochemically determined remaining discharge capacity with the active lithium inventory derived from *in situ* neutron diffraction. With this approach it is possible to differentiate several aging mechanisms, namely i) active lithium loss, ii) particle isolation, further on referred to as particle deactivation, due to loss of ionic and/or electronic contact, and, iii) destruction of bulk electrode material (metal dissolution or irreversible phase transformation). Loss of active lithium has frequently been described to occur in Li-ion cells and may have several reasons, for example ongoing SEI formation or irreversible Li-plating [32,33]. Active lithium loss can be identified if the loss of active lithium inventory measured by neutron diffraction corresponds to the electrochemically determined discharge capacity loss. The second main capacity fading mechanism is particle deactivation, resulting in an effective loss of active material. This can either be caused by the loss of ionic contact due to gassing [34], drying out [35], or pore blocking [36] or by the

loss of electronic contact due to particle delamination from the current collector [10,18] or particle cracking [37]. Particle deactivation has been observed in previous studies in aged commercial Li-ion cells by the presence of lithiated "uncharged" cathode active material [25] and/or of totally unlithiated graphite anode active material in charged cells [23,25]. The third main capacity fading mechanism is the chemical destruction of electrode active material, which could either be due to an irreversible phase transformation or to transition metal dissolution. Examples of the former are the conversion of layered LCO to spinel LCO [22] or the destruction of the spinel structure of $LiMn_2O_4$ [25] upon cycling. Phase transformations can easily be recognized by the appearance of new peaks in the neutron diffractograms which cannot be assigned to the original electrode materials. Transition metal dissolution has frequently been linked to capacity fading of Li-ion cells. It has been reported that under certain circumstances 3−4% of the iron can dissolve from LFP active material which would cause a direct and stoichiometric capacity loss [38]. If cathode active material loss due to transition metal dissolution is occurring to a significant extent, the observed lithium inventory would stay constant while the electrochemically determined remaining capacity would decrease. The dissolution of transition metals from the cathode can also indirectly contribute to the capacity fading of Li-ion cells by catalyzing electrolyte reduction at the graphite anode, causing a loss of active lithium and an increase in cell impedance [39]. As this is a catalytic process, already a very small amount of transition metal dissolution, whose corresponding direct stoichiometric capacity loss would be negligible, can cause a substantial capacity loss [40]. Note that in the framework of this study, the transition metal triggered capacity loss on the anode side would be observed as increased active lithium loss, rather than constituting an independent capacity loss mechanism.

2. Experimental

2.1. Cell information

The cylindrical 18650-type graphite/LFP prototype cells were provided by the battery producer (VW-VM Forschungsgesellschaft mbH & Co. KG, a joint venture between Volkswagen and VARTA Microbattery GmbH). Each cell consisted of a LFP cathode, an organic carbonate based electrolyte with $LiPF_6$ as conducting salt, a standard polyolefin separator, and a graphite anode made of either mesocarbon microbeads or needle coke. In both types of cells identical LFP cathodes were used. The cathode consisted of 90 wt% active material, 5 wt% binder and 5 wt% conductive additive (3 wt% graphite and 2 wt% SuperC) and was coated on both sides of an Al-foil current collector; all cells contained a total of 10.75 g LFP (2.4 wt % carbon coating), resulting in a theoretical cell capacity Q_{theo} of 1.678 Ah (based on an achievable capacity of 160 mAh g_{LFP}^{-1}, see Supporting Information). The amount of anode active material was adjusted to obtain an anode/cathode capacity ratio of 1.25 considering the specific capacities of MCMB (330 mA g^{-1}) and needle coke (349 mAh g^{-1}). The anodes consisted of 97 wt% of graphite active material, 2.5 wt% binder and 0.5 wt% conductive additive coated on both sides of a Cu-foil current collector. The BET surface area of the pure powders was 2.4 m^2 g^{-1} for MCMB and 1.9 m^2 g^{-1} for needle coke.

After the cell assembly, all cells were subjected to a proprietary formation procedure and the thus obtained preformed cells were then either stored for two years (at 20% SOC and 23 °C) or cycled for 4750 cycles (at a C rate of 1 h^{-1} at 23 °C) by the battery producer. Of each cell type, three identical cells were cycled. The observed discharge capacities for the three identical cells were always within 0.4% for both cell types, exemplifying the very good reproducibility